University of Alberta

Vanadium Recovery from Oil Sands Fly Ash

by

Preston Carl Holloway

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled VANADIUM RECOVERY FROM OIL SANDS FLY ASH submitted by PRESTON CARL HOLLOWAY in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in MATERIALS ENGINEERING.

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Abstract

The fly ash produced during the upgrading of the Alberta oil sands contains between 2.0 and 3.5 wt% vanadium, and represents a significant vanadium resource (3.6 million kilograms per year or 3.5% of total world vanadium production). Research was performed to move vanadium recovery from the oil sands fly ash towards commercialization. Salt roasting tests on Suncor ash samples collected over a 25 year period were performed to determine the effects of time, temperature, and roasting additions on vanadium recovery and the optimum salt roasting conditions for the Suncor ash. Other roasting reagents, and lixiviants, were also tested to try to improve the vanadium extractions achieved with salt roasting. Syncrude ash was treated under similar salt roasting and leaching conditions to quantify the differences between ash formation in Suncor and Syncrude's coking processes, and to optimize the roasting and leaching conditions for the Syncrude ash. Several solution purification and vanadium precipitation flowsheets were tested to determine the feasibility of producing high purity vanadium from water leach solutions. Finally, characterization of the fly ash, for the first time, allowed a good understanding of the mineralogy of the oil sands fly ash and the mechanism behind the salt roasting of the fly ash to be attained.

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1.0 Introduction

The bitumen in the Athabasca oil sands deposits in northern Alberta are known to contain appreciable amounts of V and Ni as organometallic complexes called porphyrins in the organic fraction of the oil sands (1). During processes used by Suncor and Syncrude to upgrade the bitumen and produce synthetic crude oil, the vanadium is concentrated to between 2.0 and 3.5 wt% (3.6 to 6.2% V_2O_5) in the fly ash, which is produced during combustion of the coke formed from the bitumen. Currently, approximately 250 and 50 tonnes of fly ash are produced by Suncor and Syncrude per day, respectively, representing a resource of approximately 5.6 tonnes of vanadium per day, or the equivalent of approximately 3.6 million kilograms of V_2O_5 per annum (2).

Oil sands fly ash represents a unique vanadium deposit. The fly ash has a vanadium grade roughly two to five times higher than the highest grade vanadiferous concentrates currently being processed for primary vanadium production in South Africa and Australia (3,4). Compared to other vanadium deposits, mining costs for this material would be essentially zero, as the feed material already has a fine particle size and it is produced daily during the production of crude oil from the oil sands. At current levels of production from Suncor and Syncrude, a "mine life" for the oil sands deposits is currently projected to be greater than 50 years. The deposit is also fairly large as, at current levels of world vanadium production, and current levels of oil production by Suncor and Syncrude, the vanadium contained in the fly ash would represent approximately 3.5% of total world production (2,5) (The contained vanadium could approach 7% of world production with the current upgrading programs at Suncor and Syncrude, which are expected to be completed in 2005.) The location of the deposit is also advantageous as Fort McMurray is a well-established industrial centre, providing the advantages of a trained workforce and well-established utilities and services, which would both be required for a potential vanadium production plant.

However, the fly ash produced by Syncrude and Suncor is also a unique material, both chemically and mineralogically. During combustion of the bitumen coke, mineral matter, such as clays or sand, which has not been removed during the separation of the bitumen from the sand, combines with vanadium and nickel, which are released during

the combustion of the porphyrin complexes in the bitumen. The overall bulk composition, physical characteristics and microstructure of the oil sands fly ash resemble fly ash from coal combustion, but coal fly ash seldom contains appreciable amounts of any valuable metal, with the exception of perhaps Al or Ti, to warrant investigation into metal recovery. Fly ash from the combustion of petroleum can often contain significant concentrations of vanadium and nickel, but the low levels of entrained mineral matter in the petroleum result in ashes with high concentrations of V and Ni, as their respective oxides, and low levels of impurities. This generally allows these materials to be treated readily with various hydrometallurgical processes. Thus, the ash formed during combustion of oil sands bitumen is highly complex, containing significant concentrations of Al, Fe, Ni, Si, Ti and V, and with some similarities to both coal and petroleum fly ashes.

The oil sands fly ash is also an atypical vanadium concentrate, as most of the commercially exploited vanadium ores are magnetite ores, where vanadium is present as V^{3+} in a solid solution with ferric iron in the magnetite. As such, those ores can generally be upgraded magnetically so that the resulting concentrates contain low levels of impurities, such as Al and Si. In the oil sands fly ash, aluminum and silicon are the two most abundant metals in the ash and this has made it difficult to further upgrade the ash by removing Al and Si. The aluminosilicate matrix of the oil sands ash means that the chemistry and mineralogy of the ash, and their effect on the processing of the ash with "conventional" vanadium recovery processes, are much different than would be expected for more "traditional" vanadium concentrates. The ash is also much different mineralogically from most other vanadium containing materials, including iron or titanium ores, carnotites, ferrophosphorus, clays, shales, slags or petroleum ashes, which have been tested to recover vanadium.

This thesis focuses on the recovery of vanadium, and other metals, such as Mo and Ni, from the oil sands fly ash produced by Syncrude and Suncor in northern Alberta. More specifically, this research concentrated on the areas of research that either were not addressed, or not well understood, in previous studies on this topic, in an effort to move vanadium recovery from these materials towards commercialization. Salt roasting tests were conducted for Suncor ash samples collected over a 25 year period to determine the

effects of time, temperature, and roasting additions on vanadium recovery and the optimum salt roasting conditions. Other roasting reagents, and lixiviants, were also tested to try and improve on the vanadium extractions achieved with salt roasting. Syncrude ash was tested under similar salt roasting and leaching conditions to obtain a better understanding of the differences in the coking processes that formed these ashes, and optimize the roasting and leaching conditions for the Syncrude ash. Several solution purification and vanadium precipitation flowsheets were tested to determine the feasibility of producing high purity vanadium from the leach solutions. Finally, characterization work was performed using a variety of techniques and, for the first time, a good understanding of the mineralogy of the oil sands fly ash and the mechanism behind the salt roasting of the oil sands fly ash were attained.

2.0 Literature Survey

Articles on the following topics were reviewed to provide a comprehensive background for research on the extraction of vanadium and other metals from oil sands fly ash:

a. Vanadium – Occurrence, Mineralogy, Chemistry, and Importance
b. Characterization and Structure of Coal and Oil Sands Fly Ashes
c. Salt roasting of Vanadium Containing Materials
d. Vanadium Recovery from Oil Sands Fly Ash and Coal Ash

2.1 Vanadium – Occurrence, Solution Chemistry and Importance

2.1.1 Occurrence and Mineralogy of Vanadium

The Earth's continental crust is estimated to contain an average of 150 ppm V and, thus, vanadium is present at much higher concentrations in the crust than Pb, Mo, or Cu (5). However, high grade ore deposits are relatively rare as vanadium mineralization occurs in a wide variety of geologic formations and in over 50 different minerals. The table overleaf lists several of the more common vanadium minerals, their composition and some of the main locations where these minerals are found in nature (6,7).

Most of these minerals are either oxides or silicates, which are usually finely dispersed in the host rock, and as such are generally difficult to concentrate using conventional mineral processing techniques. Accordingly, most vanadium ores contain less than 1.5% V, and, in most cases, vanadium production has to occur near the deposits to minimize the cost of transporting these low grade ores.

The exception to this are some of the vanadium sulphide and lead vanadate ores which can be concentrated by gravity separation to produce high grade concentrates for the direct production of ferrovanadium (8,9). Because of this, the rich asphaltite and vanadate deposits in Peru and Namibia, respectively, were some of the first vanadium deposits to be exploited commercially. Both deposits were depleted in the last century (8,10).

Table 2.1 Table of Common Vanadium Minerals (6,7,10)

Mineral Name	Chemical Formula	V, %	Place of Occurrence
Silicates			
Roscoelite	$KV_2(OH)_2AlSi_3O_{10}$	11.2-14.0	Colorado
Oxides			
Montroesite	(V,Fe)OOH	45.4	Colorado
Duttonite	$VO(OH)_2$	50.5	Colorado
Vanadates			
Carnotite	$K_2[(UO_2)_2V_2O_8]\cdot 3H_2O$	10.3	Colorado
Corvusite	$V_{14}O_{34}\cdot n\ H_2O$	40.8	Colorado
Descloizite	$4(Zn,Cu,Pb)O\cdot V_2O_5\cdot H_2O$	12.7	Vanadate ore (Namibia)
Fervanite	$Fe_4V_4O_{18}\cdot 5\ H_2O$	24	Colorado
Francevillite	$(Ba,Pb)[(UO_2)_2V_2O_8]\cdot 5\ H_2O$	9.9	Colorado
Hewettite	$CaV_6O_{16}\cdot 9\ H_2O$	30-40	Peru, Colorado
Mottramite	$Pb(Cu,Zn)[OH(VO_4)]$	10.5	Vanadate ore (Namibia)
Tyuyamunite	$Ca_2[(UO_2)_2V_2O_8]\cdot 5\text{-}8\ H_2O$	11.1	Colorado, CIS
Vanadinite	$Pb_4(VO_4)_3\cdot PbCl$	10.2	Vanadate ore (Namibia)
Sulphides			
Bravotite	$(Fe,Ni,V)S_2$	--	Peru
Patronite	VS_4 or V_2S_5	16.8	Asphaltites (Peru)
Sulvanite	$3Cu_2S\cdot V_2S_5$	27-52	Australia, Colorado
Sulphates			
Minasragrite	$V_2O_4\cdot 3SO_3\cdot 16\ H_2O$	16.0	Peru
Iron/Ti Ores			
Coulsonite	FeV_2O_4	46.0	Fe Ores (Africa, CIS)
Magnetite	$(Fe,V)_2O_3\cdot FeO$	<0.5-1.5	Ti-Fe Ores (S. Africa, Finland, Australia)

Vanadium in iron ores and titanomagnetites is usually present as a solid solution in the minerals, substituting for Fe^{3+} or Ti^{4+} ions (11). This precludes selective separation of the vanadium by flotation or gravity separation, but the vanadium content in titanomagnetites can often be upgraded, along with the titanium or magnetite content, by using magnetic separation to produce a magnetite concentrate (11). Smelting of the iron or titanomagnetite ores for steelmaking can also be used to produce a slag that is enriched in vanadium.

Vanadium is also present in trace amounts in various petroleum deposits as metal-porphyrin complexes (12). These molecules are stable over a wide range of temperatures and have a very low vapor pressure, and, thus, they can be concentrated in petroleum

residues during combustion. Thus, vanadium can be concentrated in coke, residues, or fly ashes produced from the combustion of crude oils and oil sands bitumen.

2.1.2 Vanadium Solution Chemistry

An E_h-pH diagram for the behaviour of vanadium in solution is provided in Figure 2.1. Vanadium can be present in either the trivalent, tetravalent or pentavalent oxidation states in solution. However, the broadest range of stability in solution is as V^{5+}.

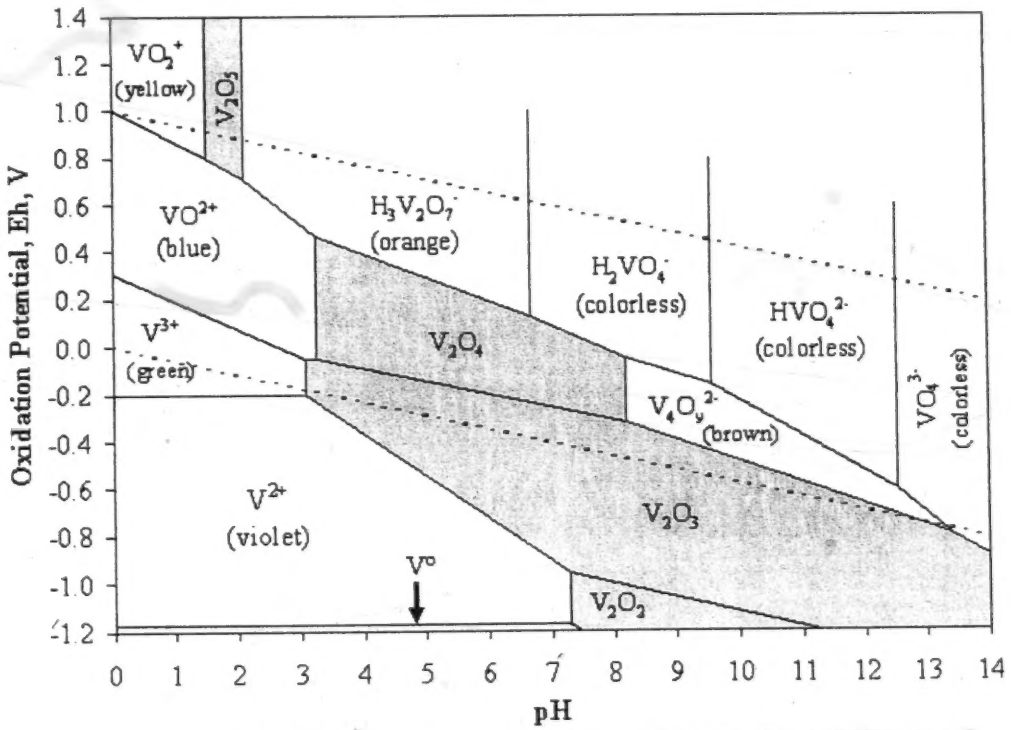


Figure 2.1 Eh-pH Diagram for Vanadium in Solution (7,13) (shaded areas represent solid phases)

As shown in the diagram, vanadium can be precipitated from neutral or slightly acidic solutions by reducing the pH to around pH 2 to precipitate a hydrated form of V_2O_5, which is know as *red cake*. Red cake is normally precipitated at 80 to 95°C as the V_2O_5 stability region increases in size with increased temperature.

$$2\ VO_3^-{}_{(aq)} + 2\ H^+{}_{(aq)} \longrightarrow V_2O_{5(s)} + H_2O_{(l)}$$

Vanadium can also be precipitated with ammonium salts from basic solutions as ammonium metavanadate (NH_4VO_3). This product can then be filtered and calcined to produce V_2O_5.

$$VO_3^-{}_{(aq)} + NH_4^+{}_{(aq)} \longrightarrow NH_4VO_{3(s)}$$
$$2\ NH_4VO_{3(s)} \longrightarrow 2\ NH_{3(g)} + V_2O_{5(s)} + H_2O_{(g)}$$

2.1.3 Uses for Vanadium

Vanadium is primarily used as an alloying agent in steels (10,12). In small quantities (0.03 to 0.08% V), vanadium is used to in high strength low alloy (HSLA) steels to improve the toughness and strength of these steels by refining the grain size and forming vanadium carbide and nitride precipitates (14,15). These steels have improved weldability and often improved corrosion resistance over many high-strength steels and, thus, are being used in applications such as oil pipelines, offshore drilling platforms and bridges (11,12,16). Vanadium is also an important additive in several classes of tool steels, with as much as 5% V being added to some high speed tool steels to produce hard vanadium carbides (14,15). Because of vanadium steel's ability to maintain its fine grain-size at elevated temperatures, vanadium is sometimes added when making heavy castings or forgings.

Vanadium is also used in several titanium alloys in the aerospace industry, with Ti-Al6-V4 as one of the more important alloys (12). The addition of vanadium improves room temperature ductility of these alloys, which, in turn, improves their workability and formability. Some vanadium alloys are also used as gettering materials in gas purification and vacuum systems (10).

Vanadium pentoxide is also used as an oxidation catalyst for the production of sulphuric acid, maleic anhydride, phthalic anhydride, acrylic acid and adipic acid from SO_2, benzene, naphthalene, propane and cyclohexane, respectively (12). Several vanadium compounds, including vanadates and vanadium chlorides, are also used as catalysts or corrosion inhibitors in the chemical industry.

Vanadium use has increased in the battery industry with greater use of Zr-V intermetallic as the cathode in some metal hydride/nickel hydroxide batteries and lithium ion batteries (12,17). Vanadium compounds are also a part of many UV absorptive or wear coatings applied in the glass and electronics industries (10). Vanadium is also used in the production of glazes, in making yellow and blue pigments (SnO_2/V_2O_5 and ZrO_2/V_2O_5, respectively), in photographic materials, and, with Eu^{3+}, in red phosphors for high pressure mercury lamps and TV screens (10). Vanadium may also have a potential market in the superconductor industry as some vanadium alloys with gallium, niobium, hafnium or zirconium have superconducting properties (10).

An emerging market for vanadium is its use in the electrolyte for the vanadium redox battery (VRB) (18). The vanadium redox battery uses the V^{3+}/V^{2+} and V^{4+}/V^{5+} reactions to produce a cell potential of about 1.26 V with a membrane separating the anolyte and catholyte. This battery is generally intended as an energy storage or load leveling device, but more recent developments have led to testing of possible automotive applications. The vanadium redox battery has several advantages over other batteries on the market as the VRB has a high energy efficiency (80 to 90%), the battery electrolyte does not degrade with time, and the use of the same element in both electrolytes minimizes the risk of cross contamination. As well, the storage capacity of the VRB is only dependent on the size of the reservoirs for vanadium solutions, and, thus, this also provides the possibility of mechanically refueling the batteries as an alternative to taking a battery offline for recharging. If demand for the vanadium redox battery increases, this could cause a considerable increase in the demand for vanadium as the entire annual V_2O_5 production of the largest South African vanadium producer would be required for the production of a single commercial size VRB (19).

2.1.4 Vanadium Pentoxide Prices

Vanadium prices are quoted commercially both for vanadium pentoxide and ferrovanadium. As much of the vanadium pentoxide is used to make ferrovanadium, the price for vanadium pentoxide will be presented here.

The average yearly prices for vanadium pentoxide from 1959 to 1998 are plotted in Figure 2.2 (20). The minimum grade for vanadium pentoxide is 98% V_2O_5, or 55% V. However, the spot price for vanadium, in the absence of free market trading of vanadium on the London Metal Exchange (LME) or other major trading exchanges, is much more volatile than the yearly prices would indicate, as illustrated in Figure 2.3 (21). This volatility is largely due to periodic under- and oversupply as a result of sporadic availability of vanadium from Russia, Kazakhstan and China. The low vanadium prices at the time of writing are connected to the slowdown in the steel industry following the September 11 terrorist attacks in the United States.

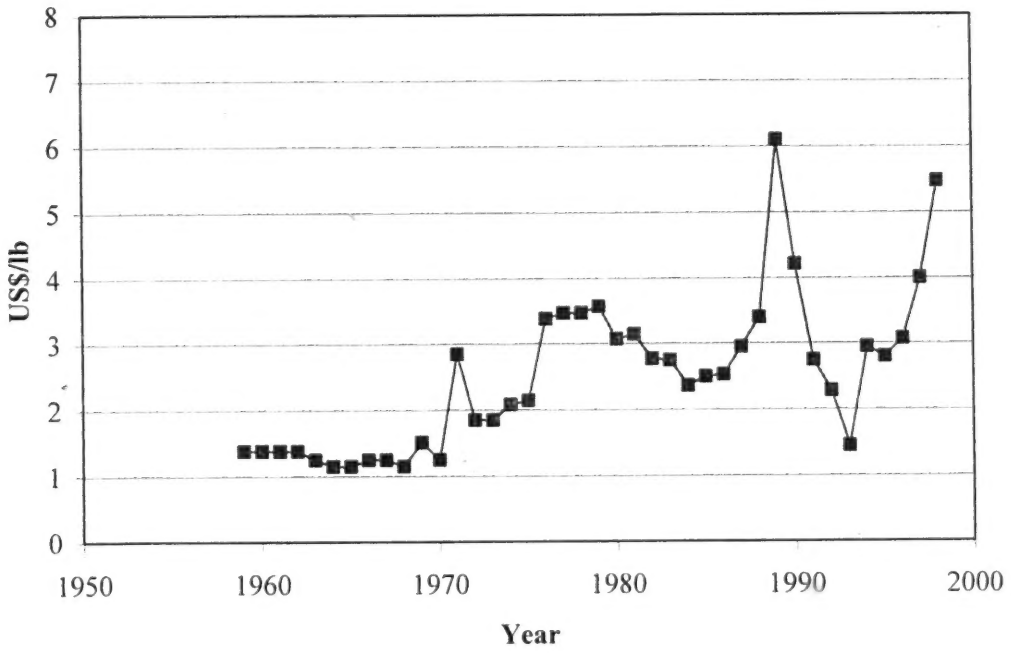


Figure 2.2 Annual Average Vanadium Pentoxide Price (US$/lb) (20)

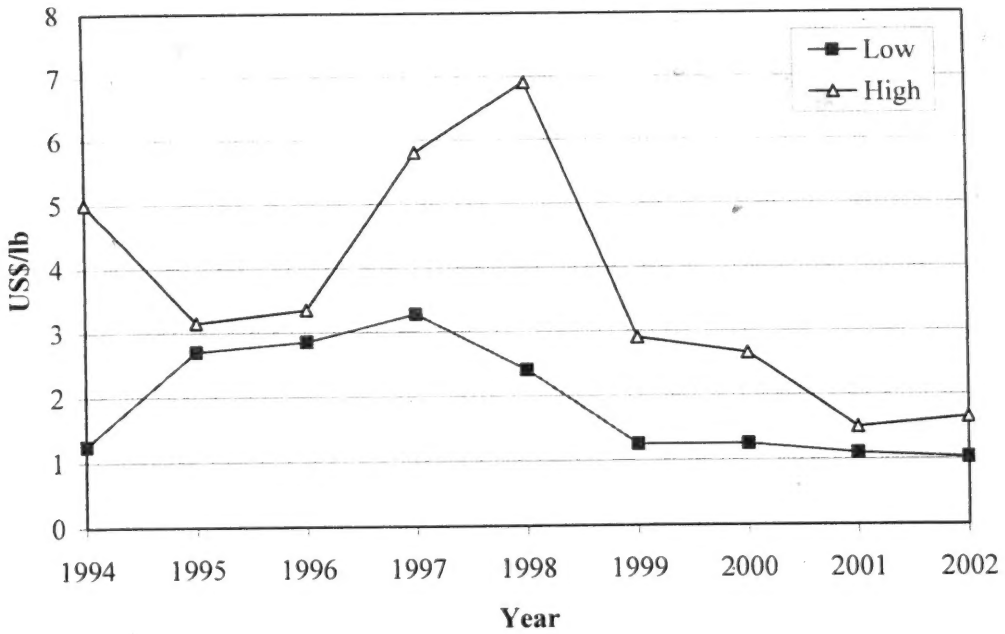


Figure 2.3 Annual Low and High Vanadium Pentoxide Prices (US$/lb) (21)

2.2 Characterization and Structure of Coal and Oil Sands Fly Ashes

2.2.1 Characterization of Coal Ash

Coal ash is formed from the transformation of mineral matter entrained in coal and is a substantial byproduct, by weight, of the combustion of coal for power generation.

The major constituents of the mineral matter found in most coals are differing amounts of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), pyrite ($FeS_2$) and calcite ($CaCO_3$), with minor amounts of quartz (SiO_2), rutile (TiO_2), illite ($KAl_5Si_7O_{20}(OH)_4$) or dolomite ($CaMg(CO_3)_2$) in some ashes. (22) Significant concentrations of other elements found in silicate rocks, including Al, Ca, Cl, Fe, Mg, K, Si, Na, S and Ti, are also present (23).

Some of these minerals then react, decompose or volatilize during coal combustion. Flagan (23) reports that dehydration of clay minerals (<225°C), oxidation of pyrite (<525°C), decomposition of sulphate and carbonate minerals to their oxides, with release of SO_2 and CO_2 gas (225-825°C), volatilization of alkali chlorides (>1075°C), and volatilization of silica (>1675°C) are possible, depending on the temperature of operation. In some cases, 4 to 8% of the mineral matter may be volatilized during combustion, possibly including the volatilization of metals such as As, Cd, Pb, Si and Zn (23).

Ashes formed at low temperatures contain minerals, such as kaolinite, illite, quartz, and dolomite, with mullite ($3Al_2O_3 \cdot 2\ SiO_2$) often forming from the aluminosilicates at higher ashing temperatures (24). Many ashes also contain significant amounts of amorphous (non-crystalline) material; tests indicate that the quantity of amorphous material varies significantly with the sample of ash and the temperature of ashing (24).

Most coal fly ash consists of a combination of unburnt carbon or char particles and, depending on the temperature and conditions of operation, irregular agglomerates or spheres of altered mineral matter from the coal. The mineral components of the coal are exposed as the carbon is burned from the coal and it is believed that the ash particles stay

attached to the organic portion of the coal as it burns (22). Thus, as the coal particle shrinks, the individual ash particles draw closer and will agglomerate or, if the temperature is high enough, melt and coalesce into spheres (22). The final size of the ash particles is dependent on the dispersion of the mineral matter through the original carbonaceous matrix and the degree of breakup of the coal particles during combustion (22,23).

Scanning electron microscopy shows that, under certain conditions, some of the spherical ash particles are hollow (Figure 2.4A). These spheres have been named "cenospheres" and have been widely reported in the fly ash from coal fired power plants (22,23,25,26). Similar particles have also been observed in the ash from the combustion of oil shale and oil sands (27,28,29). These particles are believed to be caused by gases from carbon particles that are trapped and burning inside an existing ash particle (22). This is believed to happen above 920°C, where the aluminosilicates are molten and the kinetics are more favorable, but at temperatures lower than 1120°C, so that the viscosity of the molten aluminosilicate is high enough that the trapped gases are unable to escape (23). This theory is supported by the detection of H_2O and CO_2 vapor inside the cenospheres and discovery of unburnt coal particles inside some cenospheres (26). Cenospheres are usually large (~50 μm), but, generally, account for less than 5% of the total mass of coal ash (23).

Some of the cenospheres formed have also been found to contain many small ash spheres (Figure 2.4B, 2.4D, and 2.4E) (25,26). These special cenospheres have been named "pleurospheres" (Greek "full") by some researchers. The mechanism for the formation of these structures is not well understood; the researchers who discovered the pleurospheres have proposed that their formation is a result of heating and bubbling of the gases released during combustion of the centre of the ash particle after the outer shell of the pleurosphere has already solidified (26). Conceivably, the pleurosphere structure could also be a result of mechanical entrapment of small cenospheres into broken cenospheres during handling.

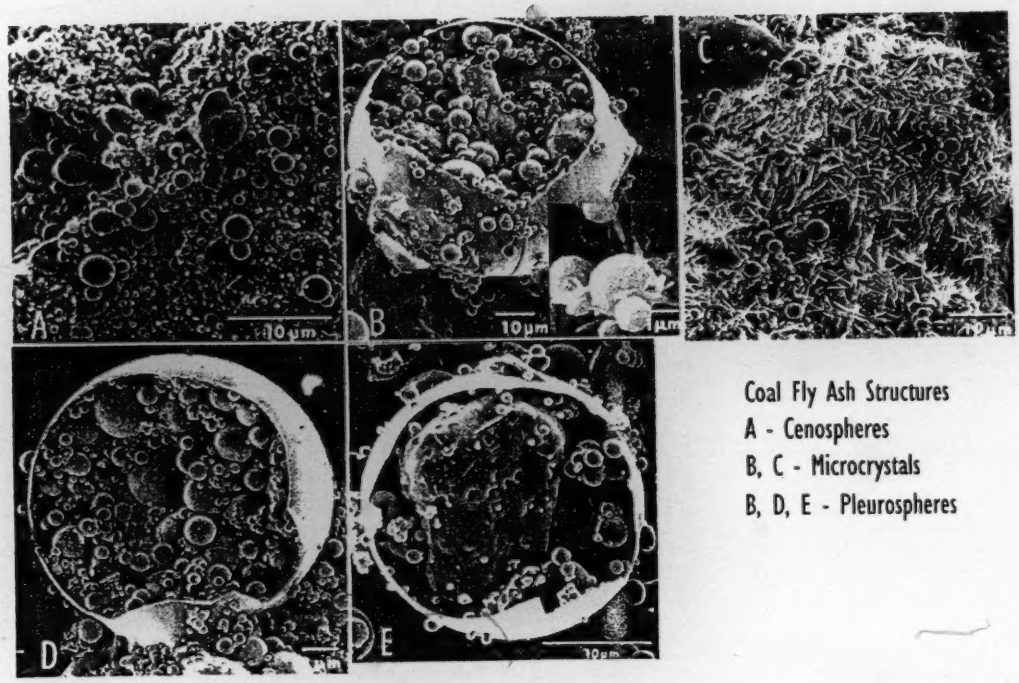


Figure 2.4 Scanning Electron Micrographs of U.S. Coal Fly Ash Samples (26)

In some cases, the formation of very small crystals, which are less than 1 μm thick in many cases, on the ash surfaces has also been observed (Figure 2.4B and 2.4C) (22,26). The formation of these crystals may be dependent on time or cooling rate as, in some cases, ash collected from bins several months after shutdown contained more crystals than freshly collected coal ash (26). In some cases, metals, such as Fe, Ti, and V, are found to concentrate in fine coal ash particles, which may represent small crystals broken off of the cenospheres (25). Other studies observe the concentration of metals, such as Cd, Cr, Co, Cu, Pb, Mo, Ni and Zn, on the surface of ash particles and propose that this phenomenon is a result of volatilization of the sulphide minerals that these metals are associated with, and subsequent condensation as their oxides onto the ash surface (30,31).

The structure of the ash particles formed during fluidized combustion of high sulphur coals in the presence of limestone ($CaCO_3$) to reduce SO_2 emissions is considerably different (32). No melting of the ash particles or the presence of a glassy phase was observed and the ash particles were irregularly shaped, probably indicating that the ash

particles agglomerated by surface adhesion in the solid state. X-ray diffraction analysis of the ashes indicated the formation of calcium silicates and aluminosilicates, such as wollastonite ($CaSiO_3$) and gehlenite ($Ca_2Al_2SiO_7$), with higher melting points than the aluminosilicate matrix in the ash formed in conventional coal combustion. No crystal formation was observed in these ashes.

The leachability of coal ashes in Toxic Characteristic Leaching Procedure (TCLP), or other similar leaching tests, is highly variable and is likely a function of the composition and mineralogy of the particular coal sampled being burned and the combustion conditions employed. Cerbus et al. (33) indicate that essentially no elements, with the exception of Ba and B, were leached to TCLP limits from one ash using a dilute nitric/sulphuric acid solution to simulate acid rain , while others indicate that high levels of As, Cr, Ni, Tl, Sr and V are dissolved under very mild (pH 5) conditions (34). Liskowitz et al. (31) report that elements with high surface concentrations, such as Cd, Cr, Cu, Pb, Mo and Zn, are leached from certain fly ashes with water. Higher temperature operation of coal boilers tended to lower the concentration of these elements on the ash surface and, thus, reduced the amounts of these elements that were leached with mild solvents (31).

2.2.2 Characterization of Oil Sands Fly Ash

Oil sands fly ash is produced during the coking or combustion of the bitumen extracted from oil sands deposits. A simplified process flowsheet for Suncor's operation which focuses on the steps involved in the production of the fly ash is shown in Figure 2.5. In recent years, inclined plate separators have begun to replace the centrifuges in Suncor's flowsheet. Centrifuges are not used at Syncrude and the bitumen is coked in a fluid coker, with only a small portion of the coke being burnt to form fly ash, and the rest of the coke being stockpiled for future use (35).

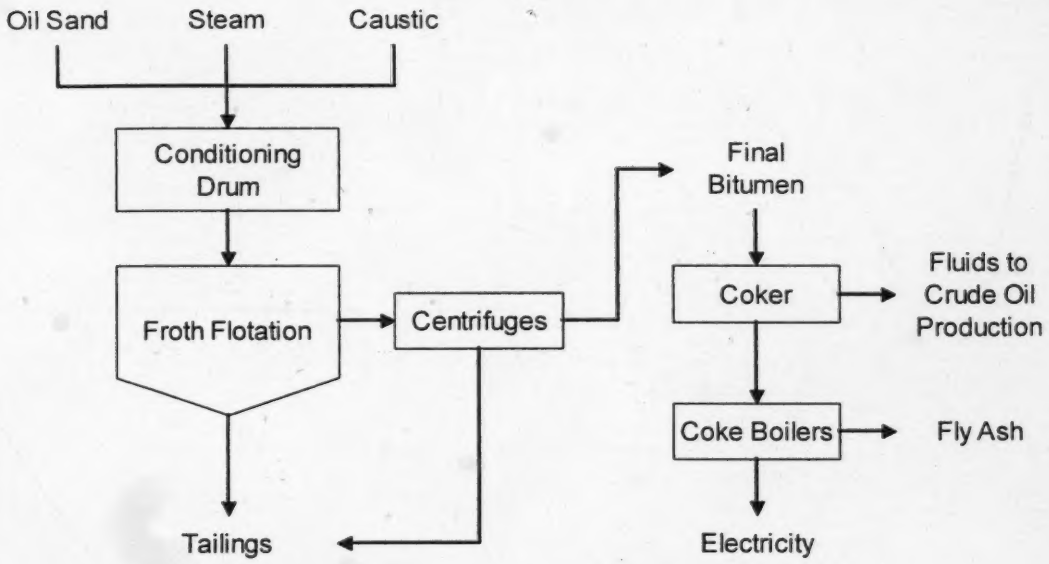


Figure 2.5 Simplified Suncor Process Flowsheet (36)

Gomez-Bueno et al. were the first group to publish a detailed characterization of the Suncor fly ash (28) The fly ash produced by Suncor is quite fine (80% <45 μm) and is made up almost exclusively of either unburnt carbon particles or aluminosilicate spheres. Some of the spheres observed were transparent while many others could be recognized as cenospheres (hollow spheres) or pleurospheres (hollow spheres filled with smaller spheres). The cenospheres are formed from the entrained mineral matter in the Suncor bitumen, which has been cited by another researcher to include quartz, potassium feldspar, muscovite, kaolinite, illite and montmorillonite (37). Some small mineral particles, likely fine sand particles entrained during bitumen recovery, and, in some cases, large numbers of very fine "microcrystals" growing on the outside of the aluminosilicate spheres were also observed in the fly ash samples (28). The finest fraction of the fly ash (<4 μm) contained higher levels of V, Ni, Ti and Fe (28).

Griffin and Etsell (29) also observed microcrystals in their Suncor ash sample. The microcrystals were between 0.1 and 0.8 μm in width and 0.5 to 5 μm in length. In addition, the crystals were shown to contain much higher levels of V, Fe, Ti and Ni than the surrounding aluminosilicate spheres. These findings led to the conclusion that the

"fine" fraction of the fly ash, reported by Gomez-Bueno et al, is likely made up largely of microcrystals that have broken off the aluminosilicate spheres (28).

Majid and Ripmeester (38) leached Syncrude and Suncor fly ash in several stages with HCl and HF to lower the ash content of the fly ash and, thus, make it more amenable to further combustion. These workers reported the dissolution of 92% of the ash content of the Suncor ash and 70% of the Syncrude ash. Between 90 and 95% of the Al, Fe, Ni, Si, Ti and V were dissolved from the Suncor ash, and 80 to 85% of the Al, Fe, Si and Ti and 35% of the Ni and V were dissolved from the Syncrude ash. This indicates that a large portion of the valuable metals in the fly ash are either present in a readily acid-leachable form or are associated with the aluminosilicate matrix of the ash.

2.3 Salt Roasting of Vanadium Ores

Roasting of vanadium materials with an alkali salt has a long history as commercial plants have been operating with variations on the salt, or alkali, roasting process since 1910. Extensive research has been conducted on salt roasting and numerous patents have been issued for the application of salt roasting to the recovery of vanadium from carnotite/roscoelite ores, iron ores, titaniferous magnetite ores, slags, ferrophosphorus and phosphorus residues, clays, shales, laterites, and petroleum combustion products, with commercial operation of salt roasting plants limited to a handful of deposits in South Africa, Australia, the United States, China, Russia, and Kazakhstan (5).

2.3.1 Chemistry of Salt Roasting

In brief, salt roasting involves the reaction of sodium chloride with vanadium and water vapor and/or oxygen to form sodium metavanadate, or a similar water soluble vanadium compound, depending on the valence of the vanadium in the ore (11,39).

$$2\ NaCl + V_2O_5 + H_2O \rightarrow 2\ NaVO_3 + 2\ HCl$$
$$2\ NaCl + V_2O_4 + H_2O + \tfrac{1}{2}\ O_2 \rightarrow 2\ NaVO_3 + 2\ HCl$$
$$2\ NaCl + V_2O_3 + H_2O + O_2 \rightarrow 2\ NaVO_3 + 2\ HCl$$

If water is absent, the reaction forms Cl_2 instead of HCl, and more oxygen per reaction is required, as in the example shown below.

$$2\ NaCl + V_2O_5 + \tfrac{1}{2}\ O_2 \rightarrow 2\ NaVO_3 + Cl_2$$

The reactions of the vanadium oxides with sodium sulphate and sodium carbonate are similar, but water vapor, and in some cases, oxygen, is not required in the reactions.

$$Na_2SO_4 + V_2O_5 \rightarrow 2\ NaVO_3 + SO_2 + \tfrac{1}{2}\ O_2$$
$$Na_2SO_4 + V_2O_4 \rightarrow 2\ NaVO_3 + SO_2$$
$$Na_2SO_4 + V_2O_3 + \tfrac{1}{2}\ O_2 \rightarrow 2\ NaVO_3 + SO_2$$

$$Na_2CO_3 + V_2O_5 \rightarrow 2\ NaVO_3 + CO_2$$
$$Na_2CO_3 + V_2O_4 + \tfrac{1}{2}\ O_2 \rightarrow 2\ NaVO_3 + CO_2$$
$$Na_2CO_3 + V_2O_3 + O_2 \rightarrow 2\ NaVO_3 + CO_2$$

In the presence of some calcium or magnesium compounds, the vanadium oxides can react with calcium or magnesium to form calcium or magnesium vanadates that are insoluble in water. The following shows the reactions between lime and vanadium pentoxide to form calcium pyrovanadate ($Ca_2V_2O_7$) and calcium orthovanadate ($Ca_3(VO_4)_2$), both of which have vanadium solubilities in water of less than 1 g/L (11).

$$2\ CaO + V_2O_5 \rightarrow Ca_2V_2O_7$$
$$3\ CaO + V_2O_5 \rightarrow Ca_3(VO_4)_2$$

In some cases, iron and aluminum are also believed to react with vanadium to form insoluble iron or aluminum vanadates.

Vanadium bronzes, such as NaV_6O_{15}, can be formed if not enough salt, moisture or oxygen is present in the roast, especially for materials in which some vanadium is present as V^{3+} or V^{4+} (11). The following is an example of these types of reactions.

$$NaCl + \tfrac{1}{2}\ V_2O_4 + {}^{5}/_{2}\ V_2O_5 + \tfrac{1}{2}\ H_2O \rightarrow NaV_6O_{15} + HCl$$

Vanadium bronzes contain vanadium both as V^{4+} and V^{5+} and are very insoluble in water.

2.3.2 Carnotite/Roscoelite Ores

Prior to 1945, carnotite and roscoelite deposits in the United States were mined and processed primarily for their vanadium content, mostly using variations on the salt roasting process. However, with the advent of atomic weapons and nuclear power in 1945, the uranium content of these ores made them a primary source for uranium, with vanadium now being recovered as a byproduct of uranium recovery. Currently, most producers in the carnotite fields in Colorado employ various acid or alkali leaching processes, without prior salt roasting, to extract uranium, with vanadium produced as a byproduct, often at lower than optimum recoveries (7).

2.3.2.1 Roasting and Leaching Conditions

Based on the available literature (7,9,40-58), roasting temperatures for carnotite/roscoelite ores are generally between 750 and 850°C with the addition of 5 to 15% NaCl, or another sodium salt. Sodium chloride, sometimes with small additions of Na_2SO_4, was generally more selective than sodium carbonate in forming sodium-vanadium compounds from these ores. Sodium carbonate tended to react with Al, P and Si to form sodium compounds, meaning that higher additions of Na_2CO_3 were required for similar vanadium extractions (53). Generally, vanadium extractions of 70 to 80% are reported for water leaching, with vanadium extraction of up to 93% reported with alkali or acid lixiviants.

Burwell indicates that the chemical reactions during salt roasting go through two stages: first, an initial reactive period, where the conversion of vanadium to sodium vanadate, $CaCO_3$ to $CaCl_2$ and some of the silica to $NaSiO_3$ takes place, and, second, an oxidation stage in which Cl_2 and HCl are released, $CaCl_2$ is converted to CaO and $NaSiO_3$ is converted to less soluble sodium or calcium silicates (53). Thus, shortened roasting times can, in part, contribute to the formation of soluble silica compounds, which, in turn, can lead to losses in vanadium recovery for a given addition of sodium salts.

2.3.2.2 Behaviour of Impurities

The presence of high levels of calcium in the carnotite/roscoelite ores generally led to reductions in the amount of water-soluble vanadium, as calcium forms vanadates that are insoluble in water, but soluble in weak acids or bases. Some processes addressed this problem by using acid or alkali lixiviants to extract vanadium from high calcium ores. (40,41,45) Others added reactive materials, such as pyrite or $FeSO_4$, to react with the calcium in the ore to produce Ca-Fe silicates or $CaSO_4$ (53). Some tests indicate that the presence of calcium as $CaSO_4$ does not hurt the recovery of vanadium, if alkali leaching is used, for some low calcium ores, but also showed that $CaSO_4$ was an ineffective reagent for high calcium ores (6% Ca) (51,52). One report indicated that $CaH_4(PO_4)_2 \cdot H_2O$ could be added to fix calcium so that sodium could react to form water soluble vanadium compounds (42).

High concentrations of iron in carnotite ores can result in the formation of much soluble silica ($NaSiO_3$) during roasting (53,54). As well, high levels of iron or aluminum in the ores can lead to the formation of water- and acid-insoluble iron-aluminum-vanadium silicates, especially as the roasting temperature or time is increased (53).

The presence of carbonaceous material significantly decreased the amount of water-soluble vanadium, likely as a result of the reduction of vanadium from V^{5+} to V^{4+} either by solid carbon or the off gases released during salt roasting (52,53).

Uranium is present in these ores at between 1 and 4%; as a result, various leaching strategies were employed to recover both uranium and vanadium. In some cases, the ores were preleached with sulphuric acid to remove much of the uranium prior to alkali roasting (40,41) or the alkali roast residue was pressure leached with Na_2CO_3 (44). Uranium extractions of between 95 and 99% were reported (40,51,52). In another case, acid leaching of the ore solubilized the uranium, and some of the vanadium, and, after stripping the solution to recover the uranium, the barren solution was used to leach the salt roast residue to improve vanadium recoveries (41).

2.3.2.3 Oxidation State of Vanadium

Vanadium in the sandstone deposits in Colorado can be present as V^{5+} in carnotite or as V^{4+} substituted for Al^{3+} in the octahedral layers of the phyllosilicate minerals, such as mica and chlorite, associated with these deposits (11). Thus, oxidation may be required to achieve high extractions from these vanadium deposits.

2.3.2.4 Economics

Vanadium from carnotite ores is now exclusively produced as a byproduct of the production of uranium from these ores, and, as such, salt roasting of carnotites for primary vanadium production is generally no longer considered economical.

2.3.3 Iron Ores

Alkali roasting has also been applied to vanadium recovery from iron (magnetite) ores (11,59,60-73) These ores generally contain low levels of vanadium, with the ores cited in the literature containing less than 1.1% V, and usually less than 0.6% V.

2.3.3.1 Roasting and Leaching Conditions

Salt roasting of iron ores is conducted at relatively high temperatures (1100 to 1300°C). These roasting temperatures are much higher than the melting point of NaCl and, as a result, NaCl can melt and cause agglomerations, or "ringing", in the kilns at these temperatures (67,68). Sodium carbonate tends to attack the spinel structure of the ore more aggressively than Na_2SO_4 and can cause more impurities to report to the leach solutions (11,59). Thus, Na_2SO_4 or Na_2CO_3-Na_2SO_4 mixtures are generally considered the best sodium salt for roasting iron ores as Na_2SO_4 is quite reactive at high roasting temperatures (11,19).

Vanadium extractions as high as 96% are cited for additions of up to 5% Na_2SO_4, while extractions of only 80 to 90% are reported for similar weights of NaCl or Na_2CO_3. (Sodium bicarbonate was tested in two papers, but alkaline leaching and $NaHCO_3$

additions of 30% were required for high vanadium extractions (59,66).) Though water was the lixiviant of choice for roasted iron ores, one report indicated that acid washing of the roast residue improved the vanadium extraction by about 10% (64).

Vanadium recovery from iron ores, before smelting to recover iron, is not generally practiced in industry as the residual sodium in the alkali roast residue can cause serious problems if the residue is smelted to produce pig iron (11). Thus, the addition of CaO or $CaCO_3$ to the iron ore, followed by roasting and Na_2CO_3 leaching, has been proposed as an alternative to salt roasting, as calcium in the roast residue does not negatively affect pig iron production (70,71,73).

2.3.3.2 Behaviour of Impurities

Iron is the major component in the iron ores and it is largely inert to the salt roasting reactions and subsequent water leaching (11).

Using Na_2CO_3 as a roasting reagent can lead to the dissolution of impurities, such as Al, Cr or Si, which can either hurt vanadium recoveries or contaminate the vanadium pentoxide produced after salt roasting (11,59).

2.3.3.3 Oxidation State of Vanadium

Vanadium substitutes for Fe^{3+} in magnetite (11). During roasting at 1100 to 1300°C, ferrous iron in the magnetite is converted to ferric oxides, such as hematite (Fe_2O_3). This change in mineralogy frees vanadium from the magnetite (spinel) structure and allows it to react with the sodium salts to form water soluble vanadium compounds.

2.3.3.4 Economics

Generally, vanadium-bearing iron ores are first smelted to recover iron as pig iron and concentrate vanadium in a vanadium-rich slag, which can subsequently be treated by salt roasting to recover vanadium.

2.3.4 Titaniferous Magnetites

Titaniferous magnetites are iron ores that contain high levels of titanium, with the titanium generally present as finely disseminated ilmenite ($FeTiO_3$) or ulvöspinel (Fe_2TiO_4) grains and the vanadium substituting for iron in the magnetite structure (74). Generally, these ores cannot be treated in conventional iron blast furnaces as the titanium can react with carbon and nitrogen in the blast at high temperatures to form titanium cyanide which forms accretions in the furnace shaft (8). Thus, smelting of the titanomagnetites ores to produce a Ti-V slag is not always possible and vanadium recovery requires direct treatment of the titanomagnetite.

Numerous studies have been performed on various titanomagnetite samples and the results of these studies are summarized in the sections below (8,9,73,75-108).

2.3.4.1 Roasting and Leaching Conditions

Sodium chloride, sodium carbonate and sodium sulphate have all been proposed as reagents for salt roasting of titanomagnetite ores, but the roasting temperatures and additive amounts vary depending on the salt used. Roasting with NaCl uses additions of 4 to 15% NaCl and temperatures ranging from 800 to 1100°C, while Na_2CO_3 additions of 7 to 50%, but usually between 10 and 20%, and roasting temperatures of 850 to 1200°C are cited for sodium carbonate. Roasting with Na_2SO_4 is conducted at high temperatures (1200 to 1300°C) with additions of 5% Na_2SO_4 cited for ores from Finland, Russia and India and up to 12% reported for some South African ores (11). In commercial practice, however, Na_2SO_4, or Na_2CO_3-Na_2SO_4 mixtures are generally considered the best sodium salt for roasting titanomagnetites as Na_2SO_4 is quite reactive at the high roasting temperatures adopted by most commercial vanadium plants (11,19).

The addition of other reagents, such as $(NH_4)_2SO_4$, FeS_2, and S along with NaCl to improve vanadium extractions has also been proposed (79), as has the addition of limestone ($CaCO_3$) or fluorspar (CaF_2) (73,82,83,86,99). The first set of additives did not offer significant improvements over roasting with NaCl alone and the calcium-based

additives formed calcium vanadate compounds and required weak acid or alkali solutions to give extractions greater than 80%.

Water is the preferred lixiviant for leaching vanadium from roasted titanomagnetite ores, but, in some studies, leaching with Na_2CO_3, NaOH and HCl was used to improve vanadium extractions (82,88,96,99). Vanadium extractions ranging from 73 to 99% are reported.

Roasting of the titanomagnetite ores was conducted in the presence of air or oxygen, as vanadium must be oxidized in the titanomagnetite from V^{3+} to V^{5+} to produce water soluble vanadium. Preoxidation of magnetite at lower temperatures (700 to 900°C) before salt roasting was used in some tests to maximize the vanadium extraction (11). Roasting in pure oxygen in another test reduced roasting times to as low as 10 minutes (97,100). These results may indicate that oxidation of vanadium is the rate limiting step in the reaction of vanadium with the sodium salts to produce water soluble vanadium.

2.3.4.2 Behaviour of Impurities

Generally, titanomagnetite ores can be crushed and upgraded magnetically with the majority of the vanadium reporting to the magnetic fraction (81). As a result, silicon is generally not a concern when processing titanomagnetites as quartz can usually be rejected from vanadium during magnetic separation. However, when the quartz is fine grained and, thus, more difficult to separate without very fine grinding, the presence of silica during roasting can lower the vanadium extraction, especially at the high temperatures used for titanomagnetites. The silica will consume sodium salt, leaving less salt available for reaction with vanadium, and complex silicates, like aegerine ($NaFe(SiO_3)_2$), can be formed which incorporate vanadium into their structures (11). The addition of Al_2O_3 to the alkali roast to form aluminosilicate compounds has been suggested to minimize the harmful effects of silicon on the vanadium extraction (82,99).

Chromium is also present in some titanomagnetite ores, where it substitutes for Fe^{3+} in the magnetite lattice, or, at higher Cr concentrations, occurs as the mineral chromite

($FeCr_2O_4$). Roasting with Na_2CO_3, or with high additions of other sodium salts, causes chromium to be leached, which can, in turn, cause contamination of the vanadium product or environmental problems with the disposal of waste solutions (82,84,87,88,98,99,106). Several researchers have proposed flowsheets which employ either selective precipitation or a combination of solvent extraction and crystallization steps to recover chromium as Cr_2O_3 or chromate crystals to minimize this problem (87,88,96,106).

In some case, large additions of sodium salts, especially Na_2CO_3, cause significant amounts of aluminum to be dissolved during leaching (88,95,96).

The levels of impurities, other than Cr, in the leach solutions sometimes require ion exchange or solvent extraction circuits to ensure that high purity V_2O_5 is produced during vanadium precipitation (88,93,95). In particular, the presence of excess sodium in V_2O_5 is cited to cause severe fuming during the aluminothermic reduction of V_2O_5 to ferrovanadium (9).

2.3.4.3 Oxidation State of Vanadium

Vanadium is largely present in titaniferous magnetites in the trivalent oxidation state, usually substituting for ferric iron in the magnetite lattice. Thus, alkali roasting of titaniferous magnetites requires the vanadium values to be oxidized to form V^{5+}, followed by reaction of the sodium salts with the vanadium to form water soluble compounds. This may require the oxidation of Fe^{2+} in the magnetite matrix (11).

2.3.4.4 Economics

Currently, production of vanadium from titanomagnetites is done commercially from five deposits: three in South Africa, one in Australia and one in China (4).

However, the vanadium grade of the titanomagnetite ore is essential to the economics of salt roasting to recover vanadium. As early as 1962, it was reported that vanadium

grades for titanomagnetite ores would have to exceed 1.6% V_2O_5 to make the processing of the titanomagnetite economical and this statement appears to be true forty years later (8). Based on that observation, only the concentrates from South Africa, grading 1.5 to 2.0% V_2O_5, would be commercially viable, with the lower grade concentrates from commercial production in Australia (1.2% V_2O_5) and China (~0.6% V_2O_5) on the borderline. (The nature of the ore deposit in Australia (i.e., a weathered magnetite in a lateritic horizon), which allows for low mining and grinding costs, improves the economics of the Windimurra deposit while sociopolitical factors likely outweigh economics in the production of vanadium in China from such low grade ores.)

With current vanadium prices, the bulk of the deposits in the United States, Finland, Canada, India and Sweden are considered to be subeconomic. The Lac Dore deposit in Quebec is one of the few deposits with high enough concentrate grades (1.4 to 1.6% V_2O_5) to warrant any serious investigation (109). However, any new primary vanadium producers would have to deal with a volatile vanadium market and heavy competition from South African producers with plants whose capital costs have long been amortized.

2.3.5 Slags

Iron and titanomagnetite ores can be smelted using in an electric furnace or blast furnace to produce pig iron. When oxygen is blown in the converter into the pig iron to remove carbon, vanadium reacts with oxygen and reports to the slag phase. Thus, the vanadium concentration is significantly concentrated in those slags, in some cases to as high as 20% V. The slag can then be granulated, mixed with an alkali salt and roasted. The high grade of some slags make them a saleable commodity and slags from the C.I.S., China and South Africa are imported to Europe and the United States for production of ferrovanadium (12).

Numerous papers have been published on the salt roasting of slags and these papers are summarized in the section below (42,97,98,110-153).

2.3.5.1 Roasting and Leaching Conditions

Roasting of slags generally requires lower temperatures than other vanadium containing materials; though temperatures as low as 600°C and as high as 1000°C are cited in the literature, most report roasting the ash at between 700 and 850°C. At these temperatures, NaCl and Na_2CO_3 are the most commonly used reagents, but some papers report successfully using sylvinite (78% NaCl, 22% KCl), NaOH, Na_2O, $NaNO_3$, Na_2SO_4, $NaHCO_3$, Na_2SiO_3, MgO, $CaCO_3$, $MgCO_3$, $Ca_3(PO_4)_2$, CaF_2 and CaO. Some slags, especially those high in Ca, Mg or P, tend to require higher salt additions, by weight, than most titanomagnetite or iron ores, but these additions were similar, or lower, per kilogram of contained vanadium. For most titanomagnetite derived slags, the salt additions were similar to those proposed for salt roasting the titanomagnetite ores, but the grade of the slags is considerably higher. Thus, smelting these materials to produce slags can provide a large savings in reagent costs during salt roasting.

Water was the primary lixiviant proposed for leaching salt-roasted slags; vanadium extractions ranged from 68 to 99% depending on the slag sample and roasting conditions. Acid leaching of the roasted slags in some studies improved the vanadium extraction from 3 to 25%, depending on the slag sample tested. (42,98,110,123,125,129,131,138). Caro's acid ($H_2S_2O_7$) was used in one paper to try to oxidize vanadium to V^{5+} during leaching (137). Vanadium extractions of only 40 to 60% were achieved, indicating that the use of an oxidizing leach was not effective in improving the vanadium extraction from the roasted slag.

As vanadium in the slags is largely present as V^{3+}, salt roasting was, in all cases, conducted in air or oxygen. Some research indicates that, though the formation of vanadates may be the rate limiting step when roasting with NaCl, the oxidation of vanadium to V^{5+} is likely the rate limiting step in the presence of Na_2CO_3 or KCl (153). As a result, roasting slag in air prior to salt roasting was found to greatly increase the amount of V^{5+} in the ore, especially at higher roasting temperatures and oxygen partial

pressures. (153) Another researcher indicates that roasting in pure oxygen with Na_2CO_3 could reduce the required roasting time to as low as 30 minutes (97).

Several researchers report that, with a slow cooling rate, vanadium may have time to form insoluble vanadium bronzes, which represent a loss of water soluble vanadium. (130,146,152). Thus, quenching the roasted slag in water is generally preferred to maximize the vanadium extraction and heat recovery from the ash.

2.3.5.2 Behaviour of Impurities

Many different strategies are reported for dealing with impurities in the vanadium slags. These include acid preleaching of highly basic slags to remove Ca, Mg or P before roasting (114,138), using Na_2CO_3 instead of NaCl for high Si slags (114), maintaining a certain SiO_2/(CaO+MgO) ratio to tie up Ca values as Ca-Mg silicates (111,122), the addition of fluorspar (CaF_2) to react with P to reduce the amount of soluble P (120), the addition of $CaH_4(PO_4)_2 \cdot H_2O$ to fix calcium and magnesium as water insoluble vanadium compounds (97), or the use of NaCl in roasting to minimize the dissolution of Fe, Cr and Mn (144). As observed in alkali roasting of titanomagnetite ores, chromium extraction tended to follow vanadium extraction in salt roasting and water leaching (133).

2.3.5.3 Vanadium Oxidation State

The vanadium in iron slags is believed to be present as spinel of the form $FeO \cdot V_2O_3$ where Mn and Mg can substitute for iron and Al, Fe^{3+} and Cr can substitute for vanadium (114). Poor separation of the slag from the iron melt and varying cooling rates can also mean that glasses, cristobalite (SiO_2), or dispersed metallic iron may also be present in the slag (149). Therefore, the vanadium is usually present in the trivalent oxidation state and, thus, must be oxidized before sodium-vanadium compounds can be formed.

2.3.5.4 Economics

Salt roasting of slags has many advantages over salt roasting of magnetite or titanomagnetite ores for vanadium recovery. Roasting of slags gave similar or higher

vanadium extractions at lower temperatures and lower reagent additions per tonne of vanadium than for roasting iron or titanium ores directly. As well, the higher vanadium grade of the slags reduces the amount of material that has to be heated and treated in salt roasting, thus, reducing the size and capital cost of the roasters required and energy requirements of the roasting process. However, the salt roasting of slags requires integration of vanadium recovery with an iron or steelmaking operation, thereby limiting the production of vanadium from slags to deposits where the production of iron or steel is also economical.

2.3.6 Phosphorus Byproducts

Vanadium is recovered commercially from ferrophosphorus that is produced as a byproduct of elemental phosphorus production from phosphatic shale in the United States by the Kerr-McGee Corporation (154-157). Several patents from this company have been issued along with several papers by other researchers on the possibility of recovering vanadium from phosphate tailings or residues (9,97,158-161). With the exception of one patent (162), all the research on recovering vanadium from phosphorus containing materials has been conducted in the United States.

2.3.6.1 Roasting and Leaching Conditions

Roasting of ferrophosphorus can be conducted at relatively low temperatures (650 to 800°C), but very high salt additions (50 to 155%) are required. This is likely due to the high vanadium content (7 to 13% V_2O_5) of the ferrophosphorus materials and the reduced oxidation state (V^{3+} or V^{4+}) of the vanadium in the ferrophosphorus. A combination of NaCl and Na_2CO_3 is often used as the use of NaCl alone is reported to form accretions on the roaster walls (159). Vanadium extractions of between 83 and 95% are generally reported.

One paper also reports making a mixture of one part ferrophosphorus to nine parts converter slag and roasting that mixture with Na_2CO_3 at 800°C in the presence of oxygen

(97). Reportedly, less than 10 minutes was required to achieve a vanadium extraction of 99% with water as the lixiviant.

2.3.6.2 Behaviour of Impurities

The presence of chloride ions in the solution from vanadium precipitation, and the corrosion associated therewith was cited as a major obstacle to recovering phosphorus from these solutions in existing phosphoric acid plants (160). To deal with this problem, and still integrate phosphorus and vanadium production, researchers and producers have suggested several options, including minimizing phosphorus dissolution by the addition of limestone or lime during salt roasting (154-157), using multistage crystallization of sodium phosphate from the vanadium solution (158,159), sacrificing vanadium extractions by roasting without any salt addition (160), or precipitating phosphorus and vanadium together as phosphatovanadic acid (PVA) (9).

2.3.6.3 Oxidation State of Vanadium

The oxidation state of vanadium in ferrophosphorus is uncertain; however, it is expected that the vanadium is in a reduced (lower) oxidation state and, thus, would have to be oxidized before it could form water soluble sodium compounds. In phosphate rock, vanadium substitutes for phosphorus in the phosphate ion and, therefore, is present as V^{5+}.

2.3.6.4 Economics

For this type of material, vanadium is only produced as byproduct of phosphate production. Thus, without the production of phosphate fertilizers from the phosphorus deposits, production of vanadium would most likely be uneconomical.

2.3.7 Clays, Laterites and Shales

Vanadium has been commercially recovered from vanadiferous clays in Arkansas by Union Carbide (11,12). (Several other researchers have published work on vanadium

recovery from clays, laterites or shales, but no other operation currently recovers vanadium commercially from these materials and, thus, these papers have been excluded from this survey (42,79,163-171).)

2.3.7.1 Roasting and Leaching Conditions

The Arkansas clays, grading about 1.7% V_2O_5, are mixed with higher grade vanadium materials, such as slags or petroleum ashes, and are roasted with 10% NaCl for 2 h at 850°C to give water leach extractions of 85% (11). The addition of 1 to 3% of materials, such as coke, charcoal, coal or petroleum residues, which contain significant amounts of carbon and vanadium, is shown to improve the vanadium extraction from the clays by up to 5% (172). In this case, vanadium can be extracted from both the clay and the petroleum residues simultaneously.

Sodalite ($Na_8(AlSiO_4)_6Cl_2$) and other sodium silicates are formed during roasting and consume some of the NaCl added to the roast; hematite (Fe_2O_3) is also formed and appears to trap some of the vanadium from the clay in its structure (11). As with carnotite ores, roasting with either Na_2SO_4 or Na_2CO_3 gave much lower extractions than roasting with NaCl.

2.3.7.2 Behaviour of Impurities

Solubilization of impurities during roasting and water leaching may be significant as solvent extraction is used to purify the leach solution from the roasted clays (11).

2.3.7.3 Oxidation State of Vanadium

In the Arkansas clays, vanadium substitutes for octahedral Al in clay minerals or for Fe in goethite (FeO(OH)) in this deposit (11). Other minerals in the clay include potassium feldspar ($KAlSi_3O_8$), quartz (SiO_2), apatite ($Ca_5(PO_4)_3(F,Cl,OH)$), pyrite (FeS_2), kaolinite ($Al_2Si_2O_5(OH)_4$), biotite ($K(Mg, Fe)_3AlSi_3O_{10}(OH)_2$), rutile ($TiO_2$) and brookite ($TiO_2$).

2.3.8 Petroleum and Coal Combustion Residues

Vanadium is commercially recovered from petroleum ash and other residues, including coal and gasification residues, from around the world. In particular, crude oils from Venezuela, some parts of the United States and Iran have particularly high levels of vanadium (12). Vanadium remains with any entrained mineral matter in the oil during combustion and, thus, tends to concentrate in fly ashes and boiler residues. In many cases, the vanadium in these combustion residues can be leached directly from the ash by acid or alkali reagents. However, the fly ash produced from petroleum products with high ash contents tend to be less amenable to direct leaching to recover vanadium, and, in those cases, alkali roasting is necessary to achieve good vanadium recoveries.

2.3.8.1 Roasting and Leaching Conditions

The composition of the petroleum residues reported in the literature is highly variable, with vanadium concentrations in the residues varying from 1.8% to 75% V_2O_5. These variations are likely dependent both on the source of the petroleum product being burned and the type of combustion process used. Extractions from these residues are, therefore, also variable with extractions as high as 99% and as low as 74% for the petroleum residues reported (97,173-183). Some of the higher grade ashes are leached with water, NaOH or Na_2CO_3 before salt roasting to remove any readily soluble vanadium and, thus, lower reagent additions in salt roasting (174,176,181).

Various reagent schemes are proposed for treating petroleum residues, including using NaCl, Na_2CO_3, NaOH, or Na_2SO_4, or Na_2CO_3-NaCl, Na_2CO_3-Na_2SO_4 or Na_2CO_3-KNO_3 mixtures as roasting additives. (Reagent additions vary widely from 10 to 250%, depending on the vanadium grade of the ash and the reagent used.) The lowest roasting temperature is reported for roasting with NaOH (400 to 500°C) (176) and the highest temperature for roasting with a Na_2CO_3-Na_2SO_4 mixture (970°C) (173).

Water was generally used as the leaching reagent, except in one paper where NaOH was used (175). In some cases, acid washing of the water leach residue was shown to improve extractions by up to 20% (177).

The literature indicates that air or oxygen atmospheres are used in salt roasting of petroleum residues. Roasting in pure oxygen, in one case, show improved kinetics with roasting times on the order of five to ten minutes being reported (97).

Only one instance of salt roasting of a coal fly ash (1% V) for vanadium recovery has been documented; an extraction of less than 60% was possible when roasting with NaCl at around 800°C (179).

2.3.8.2 Behaviour of Impurities

Due to the origin of these materials, carbon is a major impurity in the petroleum residues, with concentrations as low as 1.4% and as high as 84% reported. Several researchers indicate that the presence of carbon in salt roasting can lower the vanadium extraction, and, therefore, propose that the ashes be roasted in air before salt roasting (97,178,181).

Little information is provided on other impurities or their deportment during roasting or leaching. Significant levels of silicon in the leach solution are cited in one paper, but little other information is provided (173). Alkali or acid leaching, though, would generally be expected to dissolve more impurities than water leaching.

2.3.8.3 Oxidation State of Vanadium

Like the composition of the petroleum residues, the valence and, hence, the solubility of vanadium is highly variable and, likely, dependent on the conditions at which the residue was formed. For example, about 40% of the vanadium from a boiler slag is reportedly dissolved during grinding of the residue (176). Another paper indicated that around 60% of the vanadium could be preleached from a flexicoke residue using dilute NaOH leaching (181). Yet another researcher indicates that roasting at 900°C, followed by

leaching with sodium carbonate, could solubilize 60% of the vanadium in a particular petroleum residue (173,184). Thus, this indicates that, depending on the petroleum product being combusted and the process used to treat it, vanadium may be present either as water-soluble (i.e., fully-oxidized and already reacted with an alkali salt), alkali soluble (i.e., fully oxidized, but not converted to water soluble form) or partially oxidized vanadium (i.e., either V^{3+} or V^{4+}, but easily converted to V^{5+} in the presence of oxygen). The removal of some of the vanadium prior to salt roasting, especially for residues with very high grades of vanadium, lowered the amount of sodium salt required, thereby reducing the reagent costs for vanadium recovery by salt roasting.

2.3.9 Oil Sands Residues

The oil sands deposits in northern Alberta have also been identified as a potential resource for vanadium as vanadium is concentrated to between 3.6 and 6.2% V_2O_5 in the fly ash produced from bitumen upgrading. The residues from the combustion of oils sand bitumen are not amenable to acid or alkali leaching for vanadium recovery (28,29,185-188). The presence of entrained sand and clay particles in the oil from the oil sands is believed to "tie up" the vanadium in a glassy aluminosilicate matrix (39). At present no plant recovers vanadium commercially from oil sands residues.

2.3.9.1 Roasting and Leaching Conditions

Roasting temperatures between 760 and 905°C have been proposed, using NaCl or Na_2CO_3 as the roasting additives (28,29,39,185-192). Lower additions of NaCl than Na_2CO_3 were required to achieve high extractions when roasting Suncor fly ash.

Water was generally used as the leaching agent for these materials and this resulted in solutions containing Al, Ca, Fe, Ni and Si at parts per million concentrations. The only impurities reported to be above the ppm range are Ca, Mn, K and Na, at less than 0.7, 1, 4 and 8 g/L, respectively (29,39,185,186). One study used a sodium hydroxide leach which gave solutions containing, at the lowest, 4 g/L Si and 1 g/L Al (187,188). The rationale behind NaOH leaching of the roasted ash is unclear as NaOH leaching did not improve

the vanadium extraction over the extractions reported from water leaching (85 to 90%) by other researchers (29,39,185,186,189,190). Rapid cooling of roasted fly ash is shown to be important, as extractions from quenched and furnace cooled ash can differ by as much as 70% (39).

Roasting of oil sands residues was generally conducted in air or oxygen. However, tests indicate that roasting in nitrogen decreases the vanadium extraction slightly (39). In addition, roasting in moist air caused the ash to fuse, possibly due to partial melting of the ash under these conditions, and gave much lower vanadium extractions (39).

Extractions ranging from 67 to 99% are reported for salt roasting of cokes or ash produced by roasting bitumen coke below 600°C from oil sands bitumen (189,191,192,193,194). Significant decreases in the vanadium and nickel extractions were observed when the coking temperatures were increased above 500 to 600°C.

2.3.9.2 Behaviour of Impurities

The presence of carbon was noted by several researchers to lower the vanadium extraction (39,187-192). It is possible that carbon, or carbon monoxide produced during combustion, reduces the vanadium in these materials, thus decreasing the amount of V^{5+} available to form water soluble sodium compounds. Hence, roasting of the oil sands residues at 500 to 550°C in air, prior to salt roasting, was generally employed to maximize vanadium extractions.

As noted in Section 2.3.8.1, salt roasting and water leaching produces very pure leach solutions, with Ca, Na, Mn and K being the major impurities. Aluminum and silicon are also dissolved if NaOH leaching is used.

The levels of calcium and magnesium in these materials do not appear to be high enough to significantly affect the vanadium extraction for water leaching.

2.3.9.3 Oxidation State of Vanadium

The oxidation state of vanadium in the oil sands residue is not reported, as the mineralogy of the residues and, in particular, the fly ash samples, is not well understood.

2.3.10 Conclusions

Based on this survey of the process of salt roasting, several conclusions regarding the extraction of vanadium by salt roasting and leaching can be made. First, the salt roasting process can be, and has been, applied to a wide range of materials of remarkably different mineralogies with high vanadium extractions and relatively pure water leach solutions achieved for most materials. However, vanadium recovery from a given ore or deposit by salt roasting may not always be economical. Salt roasting is an energy intensive process, and often requires the addition of large amounts of reagents to recover very low amounts of vanadium. As a result, in many cases, vanadium is produced primarily as a byproduct of other operations, such as uranium, phosphate, titanium, or pig iron production with primary production of vanadium being limited to higher grade vanadium deposits

Second, understanding the mineralogy of the vanadium material being treated is critical to understanding its behaviour during salt roasting. Both the oxidation state of the vanadium and the host, or impurity, minerals in the vanadium ore can affect decisions on the roasting additives and the roasting and leaching conditions used in alkali roasting. Thus, certain practices used for the processing of one vanadiferous material may not be directly applicable to other vanadium ores. As well, since vanadium extractions are commonly below 100%, an understanding of the mineralogy of the vanadiferous material being processed may allow for more directed optimization of vanadium recovery for some materials.

Finally, the presence of impurities in vanadium ores can have a marked effect on the extraction of vanadium by salt roasting. In particular, the presence of carbon during roasting has been shown to lower vanadium extractions for a number of different materials and requires roasting of ores to remove carbon before salt roasting. High levels

of reactive calcium minerals in some ores have also been the source of difficulties with salt roasting, requiring the use of acidic or basic lixiviants or additional roasting reagents.

2.4 Metals Recovery from Oil Sands, Coal and Petroleum Fly Ashes

A detailed survey of the chemistry of salt roasting and its application to vanadium recovery from oil sands fly ashes is provided in Section 2.3.9. However, numerous researchers have looked at alternatives to salt roasting for recovery of metals from the oil sands fly ash. The results of these studies are discussed in the following section. (Brief descriptions on the recovery of vanadium, and other metals, from coal and petroleum ashes are also included in this section.)

2.4.1 Hydrometallurgical Processes

Vanadium and nickel can generally be readily recovered by leaching in acidic or basic media from petroleum fly ash. One example of a plant which pioneered the production of vanadium from petroleum fly ash was the Canadian Petrofina plant in Quebec which operated during the 1960's and 1970's (195,196,197). Fly ash from the steam boilers routinely contained greater than 15% V_2O_5; subsequent research led to the development of the flowsheet shown in Figure 2.6. In this process, fly ash is leached with sulphuric acid at pH 0.2 and 90°C. The vanadium in the filtered leach solution is oxidized to V^{5+} using sodium chlorate ($NaClO_3$) and the vanadium is then precipitated as red cake (hydrated V_2O_5) by adding ammonia to the solution to raise the pH to around pH 2. Extractions and precipitation efficiencies of about 95% gave an overall vanadium recovery from the fly ash of 90%.

Because of the successful recovery of vanadium from petroleum ashes, preliminary leaching testwork was conducted by several researchers to determine whether vanadium and nickel could be extracted from the oil sands fly ash with a simple atmospheric leaching process. Gomez-Bueno et al. achieved maximum vanadium extractions of 30%, 55% and 10% with H_2SO_4, NaOH, and Na_2CO_3, respectively, and nickel extractions of less than 20% for all three reagents (187,188). Griffin also tested several lixiviants, but

maximum vanadium extractions of less than 20% for acids and less than 30% for bases were reported (185). The addition of H_2O_2 improved the nickel extraction to 37%, but, generally, less than 20% of the nickel in the ash was leached using any of the lixiviants or conditions tested.

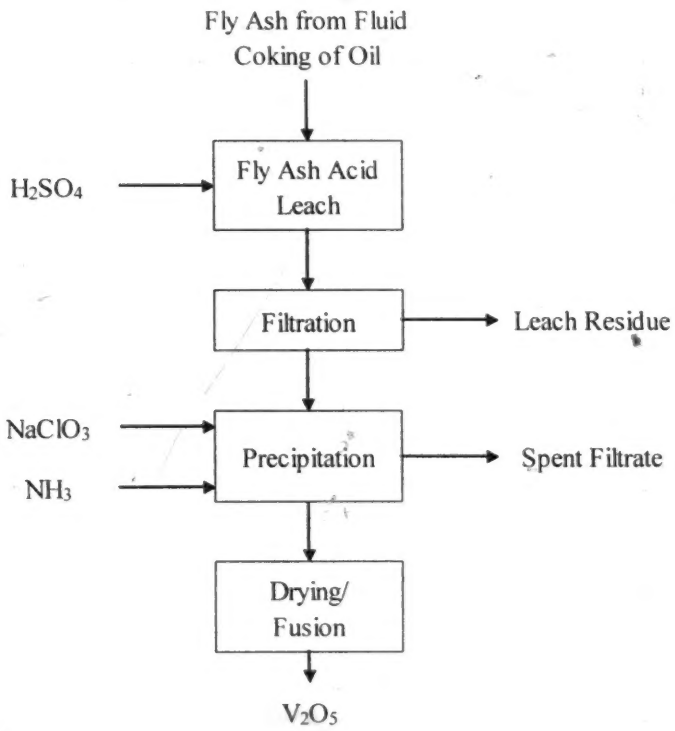


Figure 2.6 Petrofina Flowsheet (195)

Jack et al. investigated heap leaching and bioleaching of the Suncor and Syncrude coke (194,198,199). When leaching the coke with a strain of Thiobacillus thiooxidans, vanadium and nickel extractions never exceeded 30% and 40%, respectively, even after 25 days of leaching. Extractions from simulated heap leaching peaked at 15 days and never exceeding 50% V and 60% Ni. Ashing to remove carbon from the Suncor fly ash did not improve the extractions significantly with less than 40% and 21% for V and Ni, respectively, reported both before and after ashing at 500°C.

The Carbovan flowsheet is the only process to treat Suncor fly ash that has gone into commercial production (200,201). This process involves flotation to remove carbon form the ash, followed by pressure leaching with NaOH at 200°C, ion exchange to separate vanadium from the leach solution and precipitation of vanadium from the ion exchange solution by acidification as red cake. In sodium hydroxide pressure leaching, silicon dissolution is high and requires the addition of Na_2CO_3 to the leach to limit the amount of Si dissolved. The Carbovan plant was built, started up and shut down within the same year, due to low vanadium prices and the fouling of their ion exchange resin by contamination of waste oil in their process water (2,12).

2.4.2 Pyrometallurgical Processes

Several flowsheets have also been tested to determine whether the fly ash could be smelted to produce a V-rich slag, a nickel matte, ferronickel or ferrovanadium (185,202). In all the tests performed, nickel and vanadium did not report selectively to different phases in the smelting experiments. Further purification of the residues produced would be difficult, and, thus, the poor selectivity would result in unacceptable nickel and vanadium losses.

Griffin did some preliminary tests of alternative roasting conditions (185). Roasting Suncor fly ash at 800°C in air increased the vanadium extraction from the ash to as high as 54%, 30%, and 38% for H_2SO_4, NaOH, and Na_2CO_3, respectively, but nickel extractions never exceeded 2% following roasting. Poor extractions were also achieved with reduction roasting of the ash with hydrogen, chlorination of the ash, and pressure leaching of the ash, with and without the addition of SO_2 as a reducing agent (185). Roasting with 15% elemental sulphur at 900°C, followed by leaching with 10% H_2SO_4, is reported to give nickel extractions between 82 and 98% and vanadium extractions of 30 to 50% for Suncor ash (185). A much lower extraction of 55% Ni (40% V) is reported for roasting Syncrude ash under similar conditions.

Researchers at the Alberta Research Council discovered during tests to lower sulphur emissions from combustion of Suncor coke that the addition of $Ca(OH)_2$, or several other

calcium salts, to the coke during combustion drastically improved the leachability of vanadium and nickel from the resultant fly ash (193,203,204). Ashing at 900°C, with as low as 0.5% $Ca(OH)_2$, resulted in 98% V extraction in HCl, compared with only 30% without these additions. Additions of up to 5% can improve nickel extraction up to 80%. The addition of Na_2CO_3 during combustion produced similar vanadium and nickel extractions.

High vanadium and nickel extractions with acid leaching are possible if Suncor coke is ashed at temperatures less than 600°C (198,203,204). This indicates that the combustion conditions in the Suncor boilers alter the minerals in the bitumen coke so that V and Ni are harder to recover by acid leaching.

2.4.3 Metals Recovery from Coal Ash

Most studies on the recovery of metals from coal ash have focused on the recovery of Al, Si, and Ti, as the coal ash generally contains low levels of other metals (205-221). The conditions proposed for Al, Fe and Ti recovery are unlikely to be economical, compared with the price of their respective ores available on the world market. In the few instances where certain coal ashes contain V, Mo or Ni, the grade of these ashes is generally very low, and complicated flowsheets, or extreme operating conditions, are required to achieve high extractions or to combat the significant dissolution of impurity elements into the leach solutions (222-232). Leaching tests on these materials generally gave low extractions and very impure leach solutions which would require purification by ion exchange or solvent extraction before V, Mo or Ni could be recovered from solution. Overall, based on the information presented in the literature, it is unlikely that metal recovery from coal ash could be done economically.

2.4.4 Leaching of Petroleum Ashes

Studies on petroleum ash, for the most part, have been excluded from this survey as, although petroleum residues generally contain high levels of vanadium and nickel (normally as oxides), they usually contain very few deleterious impurities, such as Al, Fe or Si, and, as such, are much more amenable to leaching processes than oil sands fly ash.

3.0 Feed Materials

3.1 Fly Ash

Fly ash samples from Suncor's coking operation have been collected at the University of Alberta over the last 25 years, with the oldest samples dating from July 1977. Three samples of fly ash from Syncrude have also been obtained through Syncrude Research.

3.1.1 Chemical Analyses

Key chemical analyses of fly ash samples, after removing carbon and sulphur by roasting at 500°C, are provided in Tables 3.1 and 3.2. The combined carbon and sulphur content are referred to as loss on ignition (L.O.I.) for reporting purposes.

Table 3.1 Suncor Fly Ash Analyses, wt%

Date	V	Al	Ca	Fe	Mo	Ni	Si	Ti	L.O.I.
1977	3.02	12.2	1.11	5.33	0.17	1.00	22.8	2.02	58.6
1978	3.02	11.2	1.77	4.41	0.17	0.95	25.0	1.72	62.0
1979	2.49	13.0	0.86	3.66	0.11	0.82	23.0	1.84	35.4
1980	3.63	12.1	0.77	3.83	0.28	1.05	27.2	1.89	88.4
1982	3.58	12.7	0.80	5.63	0.23	1.12	26.2	1.65	27.3
1986	3.19	13.1	1.18	5.65	0.18	1.01	26.4	1.46	26.7
1999	3.02	11.0	1.27	5.49	0.19	0.97	25.2	1.62	58.9
2001	2.86	10.7	1.67	5.11	0.20	0.92	28.4	1.43	23.1

Table 3.2 Syncrude Fly Ash Analyses, wt%

Date	V	Al	Ca	Fe	Mo	Ni	Si	Ti	L.O.I.
Oct 98	2.10	8.19	0.82	8.93	0.24	0.66	21.0	2.24	89.5
Dec 98	1.78	5.87	2.00	3.49	0.13	0.57	36.0	1.17	50.6
2001	2.08	7.43	1.05	14.9	0.20	0.59	20.8	1.75	91.0

Detailed chemical analysis of these ash samples are shown in Table 3.3.

Table 3.3 Detailed Analysis of Fly Ash Samples

Detailed	Suncor Fly Ash								Syncrude Fly Ash		
Analysis, %	1977	1978	1979	1980	1982	1986	1999	2001	Oct 98	Dec 98	2001
Al	12.2	11.2	13.0	12.1	12.7	13.1	11.0	10.7	8.19	5.87	7.43
Ca	1.11	1.77	0.86	0.77	0.80	1.18	1.27	1.67	0.82	2.00	1.05
Cd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cr	0.06	0.06	0.06	0.07	0.06	0.05	0.06	0.08	0.06	0.11	0.05
Co	0.03	0.04	0.04	0.04	0.04	0.05	0.04	0.04	0.04	0.03	0.04
Cu	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.02	0.05	0.02	0.04
Fe	5.33	4.41	3.66	3.83	5.63	5.65	5.49	5.11	8.93	3.49	14.9
Mg	0.41	0.39	0.33	0.33	0.37	0.40	0.38	0.41	0.37	0.35	0.30
Mn	0.12	0.11	0.08	0.08	0.13	0.13	0.14	0.12	0.24	0.09	0.29
Mo	0.17	0.17	0.11	0.28	0.23	0.18	0.19	0.20	0.24	0.13	0.20
Ni	1.00	0.95	0.82	1.05	1.12	1.01	0.97	0.92	0.66	0.57	0.59
K	0.88	0.68	0.92	0.86	0.83	1.03	0.97	0.86	0.66	0.79	0.46
Si	22.8	25.0	23.0	27.2	26.2	26.4	25.2	28.4	21.0	36.0	20.8
Na	0.57	0.44	0.41	0.34	0.59	0.78	0.64	0.63	0.41	0.87	0.55
Ti	2.02	1.72	1.84	1.89	1.65	1.46	1.62	1.43	2.24	1.17	1.75
V	3.02	3.02	2.49	3.63	3.58	3.19	3.02	2.86	2.10	1.78	2.08
Pb	0.09	0.08	0.08	0.07	0.07	0.08	0.08	0.07	0.07	0.06	0.07
Zn	0.07	0.05	0.06	0.04	0.05	0.08	0.07	0.07	0.10	0.06	0.08
L.O.I., %	58.6	62.0	35.4	88.4	27.3	26.7	58.9	23.1	89.5	26.7	91.0

3.1.2 Characterization

Several samples of Suncor and Syncrude ash were examined using the scanning electron microscope (SEM). X-ray diffraction patterns for these samples were also generated and used to identify the predominant minerals present in the as-received fly ash.

3.1.2.1 Suncor Ash

Figures 3.1 to 3.4 show the 1979, 1980 and 1982 samples of Suncor ash after roasting at 500°C to remove carbon from the ash. Pictures were taken at magnifications of 150, 500, 1500 and 4000x.

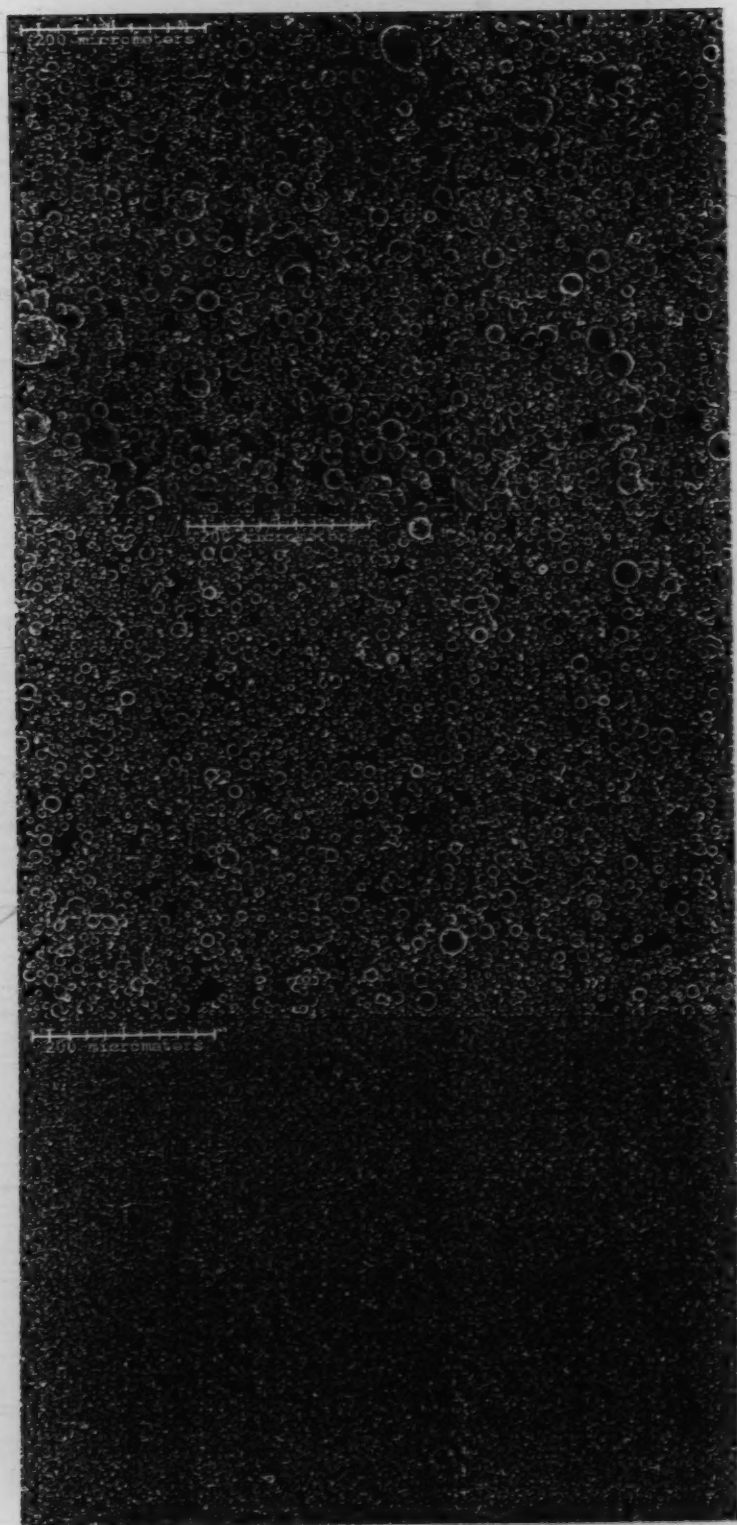
The mineral portion of the Suncor fly ash is made up predominantly of aluminosilicate cenospheres, the size distribution of which varies depending on the ash sample, as shown at low magnification (Figure 3.1). These spheres are much smaller (2 to 30 μm) than those seen in coal ash samples (23). Some of the cenospheres in the ash samples are not perfectly spherical, and pleurospheres (i.e., hollow spheres containing smaller cenospheres) are also observed. Though the surface of most of the spheres is quite smooth, at higher magnifications some cenospheres appear to have a rough coating which is similar in appearance to the rough material visible in the spaces between some of the spheres. EDX analysis indicated that this material had a similar Al and Si content, but was slightly enriched in Fe and Ti compared with the surrounding spheres. This may indicate that, even at a given set of boiler conditions, not all the mineral matter in the ash forms the cenospheric structures predominantly observed in the ash samples. The abundance of this aluminosilicate phase, containing Al, Ca, Fe, Ni, Si, Na, Ti and V, indicates that the majority of the mineral components entrained in the bitumen are combined into a single phase during combustion of the bitumen.

X-ray diffraction (XRD) patterns of this sample indicated that the structure of the cenospheres was poorly crystalline, but low intensity peaks corresponding to mullite ($3\ Al_2O_3 \cdot 2\ SiO_2$) can be identified. This could indicate that the cenospheres are composed of a metastable aluminosilicate glass, with small quantities of high-

temperature crystalline aluminosilicates contained therein. The presence of trace amounts of mullite would normally indicate that the minimum boiler or coking temperature in Suncor's operations was 1200°C or higher, depending on the original mineralogy of the ash before coking (233). However, more recent studies looking into the phase reactions during firing of V-doped clay bricks indicate that, in the presence of vanadium, mullite, and several other high temperature compounds, can form at much lower temperatures (234). The short retention times and fast cooling rates in the boilers are likely the cause of the high degree of poorly crystalline material in the ash; a more crystalline structure would be expected at longer retention times or slower cooling rates.

In the 1979 and 1980 samples, elongate crystals, containing Ca and S, were also identified and are believed to be anhydrite ($CaSO_4$). Contrary to previous reports of the presence of microcrystals in as-received fly ash, no sign of fine acicular crystals containing high concentrations of Fe, Ti, Ni or V were observed (29,185,186).

Overall, though, the Suncor ash shows a low degree of variability from sample to sample. Most of the components of the mineral fraction of the ash are present as a single glassy aluminosilicate phase, with only minor amounts of secondary phases observed.

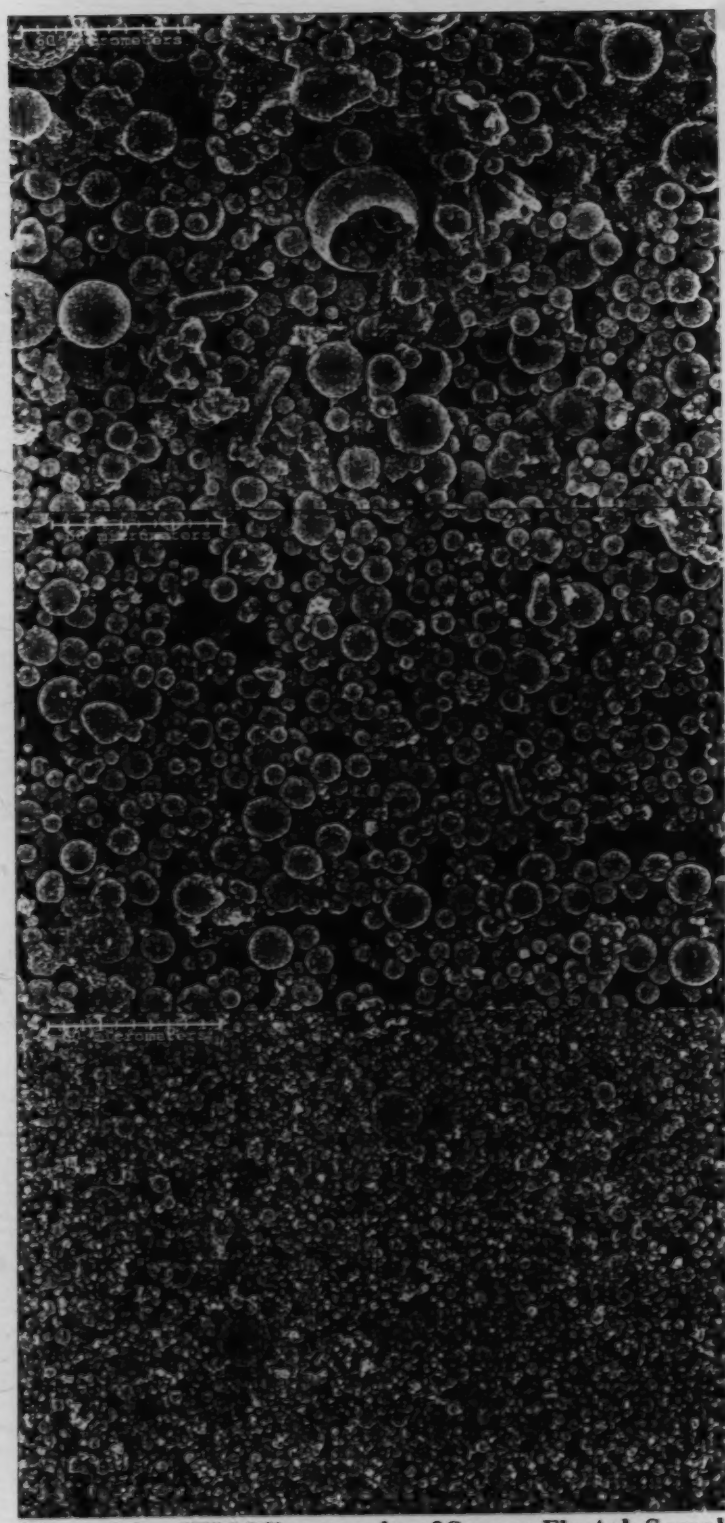


Suncor Aug 1979
150x Magnification

Suncor Mar 1980
150x Magnification

Suncor Mar 1982
150x Magnification

Figure 3.1 SEM Micrographs of Suncor Fly Ash Samples (150x Magnification)

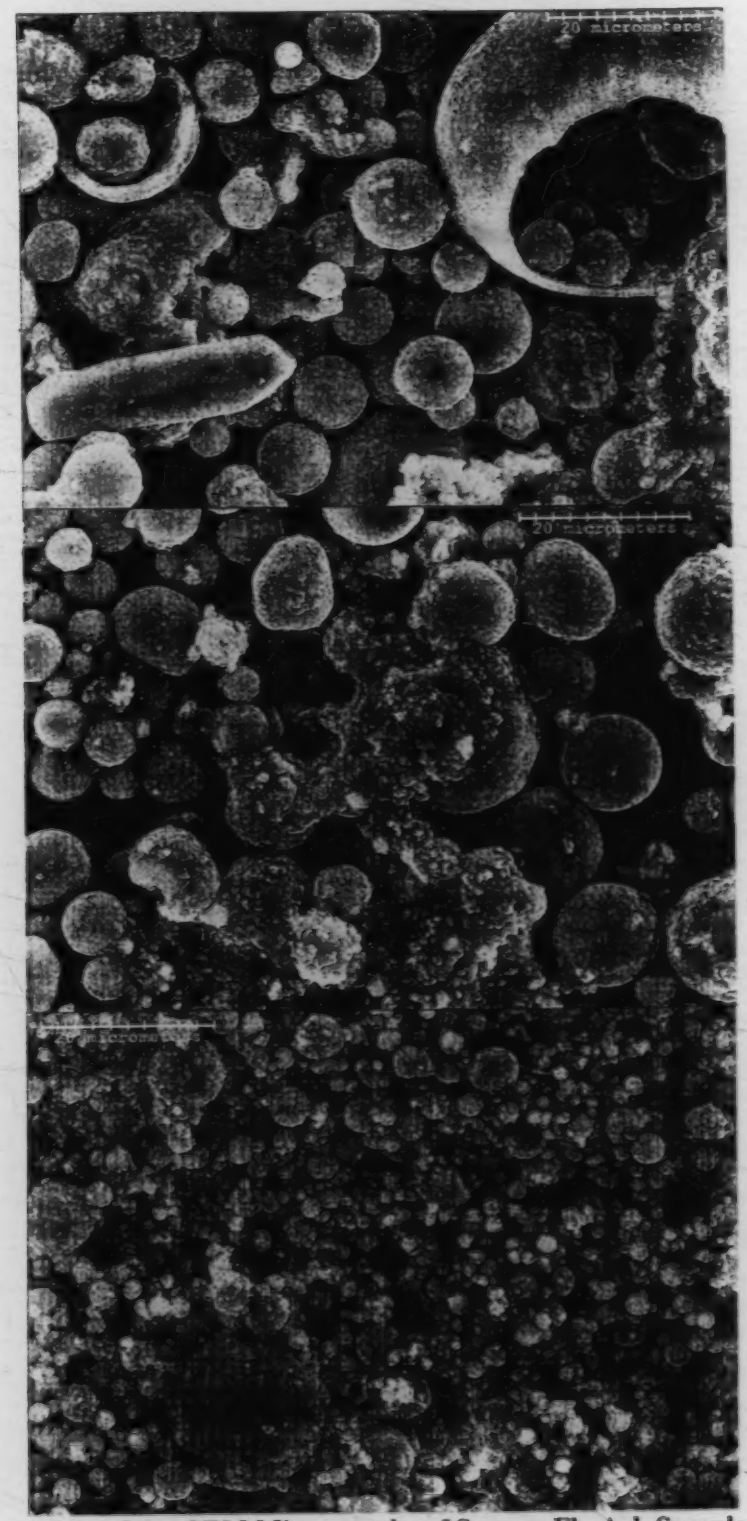


Suncor Aug 1979
500x Magnification

Suncor Mar 1980
500x Magnification

Suncor Mar 1982
500x Magnification

Figure 3.2 SEM Micrographs of Suncor Fly Ash Samples (500x Magnification)

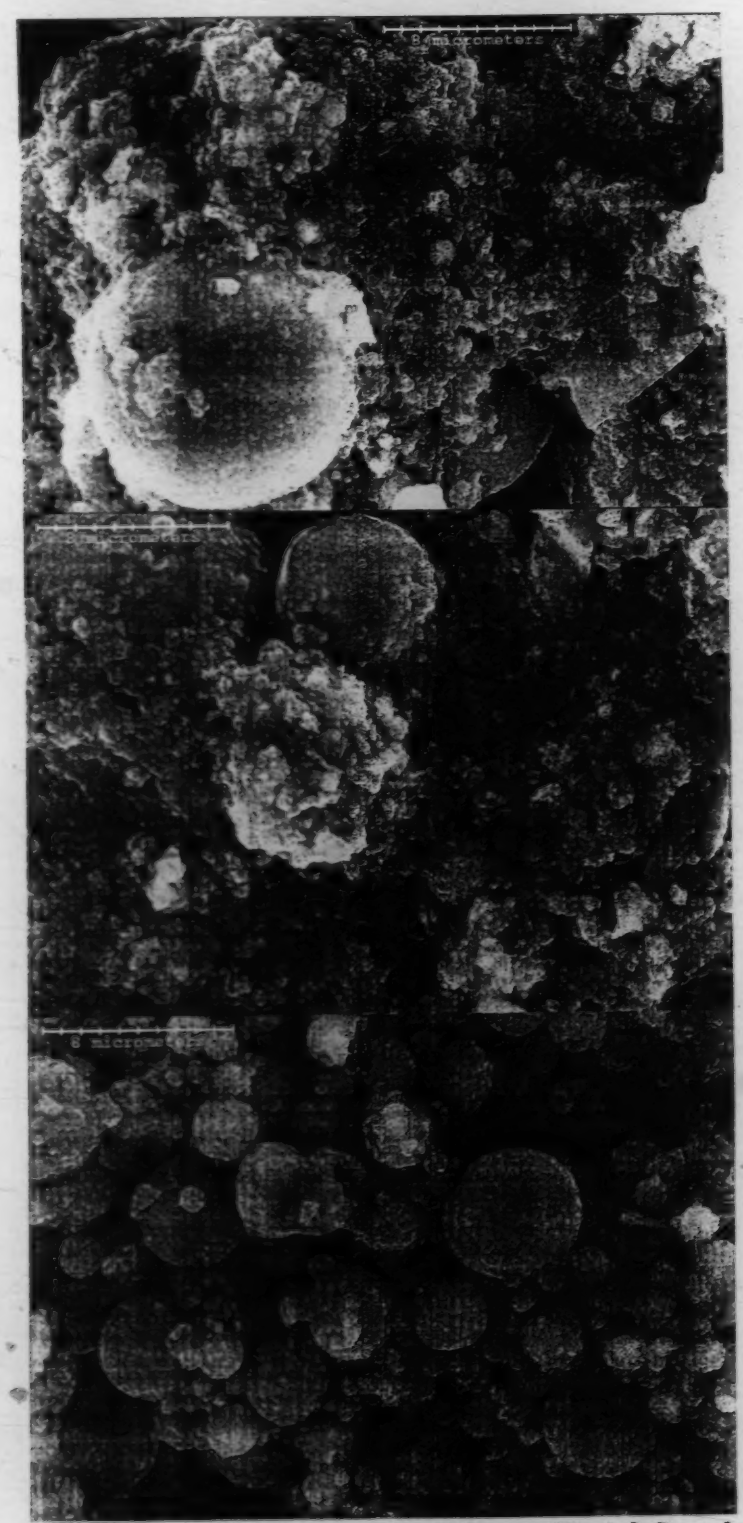


Suncor Aug 1979
1500x Magnification

Suncor Mar 1980
1500x Magnification

Suncor Mar 1982
1500x Magnification

Figure 3.3 SEM Micrographs of Suncor Fly Ash Samples (1500x Magnification)



Suncor Aug 1979
4000x Magnification

Suncor Mar 1980
4000x Magnification

Suncor Mar 1982
4000x Magnification

Figure 3.4 SEM Micrographs of Suncor Fly Ash Samples (4000x Magnification)

3.1.2.2 Syncrude Fly Ash

Very little work has been done previously to characterize the Syncrude fly ash. One study showed SEM micrographs of Syncrude ash, but these micrographs were taken without removing carbon and, as such, only spherical or globular particles consisting largely of carbon were observed (185). Few observations could be made on the actual mineral matter in the fly ash from those pictures and analyses as any mineral structures present would be obscured by the high carbon content of the ash.

Figures 3.5 to 3.8 show the Dec 98, Oct 98 and Jun 01 samples of Syncrude ash after roasting at 500°C to remove carbon from the ash. Pictures were again taken at 150, 500, 1500 and 4000x magnification.

Syncrude ash shows a higher degree of variability from sample to sample than the Suncor ash (Section 3.1.2). Large (10 to 30 μm) free quartz particles are observed in all three ash samples, and they are more numerous in the two 1998 samples. Scoping tests indicated that 10 to 15% of the mass of the ash could be separated as free silica particles by centrifuging or flotation. Thus, it is likely that the free quartz in the Syncrude ash is a result of Syncrude's use of flotation as its primary process for separating bitumen from the oil sands. (Suncor uses centrifuging after flotation to separate the bitumen which would provide better rejection of the coarse silica particles from the ash.) The quartz particles appear largely unaltered from the conditions experienced in Syncrude's coking operations.

Cenospheres are present in the Dec 1998 sample, though in much lower quantities than in the Suncor ash samples, but the spheres are not visible in either of the other two Syncrude ash samples. This could indicate that the Dec 1998 ash sample was formed at higher operating temperatures and, thus, could represent a sample of ash formed during upset conditions in Syncrude's coking process. As well, the particles in the Dec 1998 sample are, generally, larger and more round in shape while the Oct 1998 and Jun 2001 samples consist largely of fine, angular particles, or agglomerates of those particles.

Microcrystals (0.5 to 1 μm thick) are also observed at high magnifications in the Dec 1998 ash sample. Particles rich in iron and sulphur, possibly pyrite or another iron sulphide, are also detected in the Oct 98 ash sample.

X-ray diffraction also shows considerable differences between the Dec 98 and the Oct 98 ash. Quartz (SiO_2) and anhydrite ($CaSO_4$) are the only identifiable crystal phases in the Dec 98 ash. Quartz (SiO_2), synthetic hematite (Fe_2O_3), pseudobrookite (Fe_2TiO_5), nickel titanate ($NiTiO_3$), and cristobalite (a high temperature SiO_2 polymorph) were identified as crystalline phases in the Oct 98 ash sample. The XRD patterns for both materials, though, largely showed small broad peaks that are characteristic of materials containing a large amount poorly crystalline phases. No crystalline aluminosilicate phases, or vanadium-bearing phases, were identified from the XRD patterns of either sample.

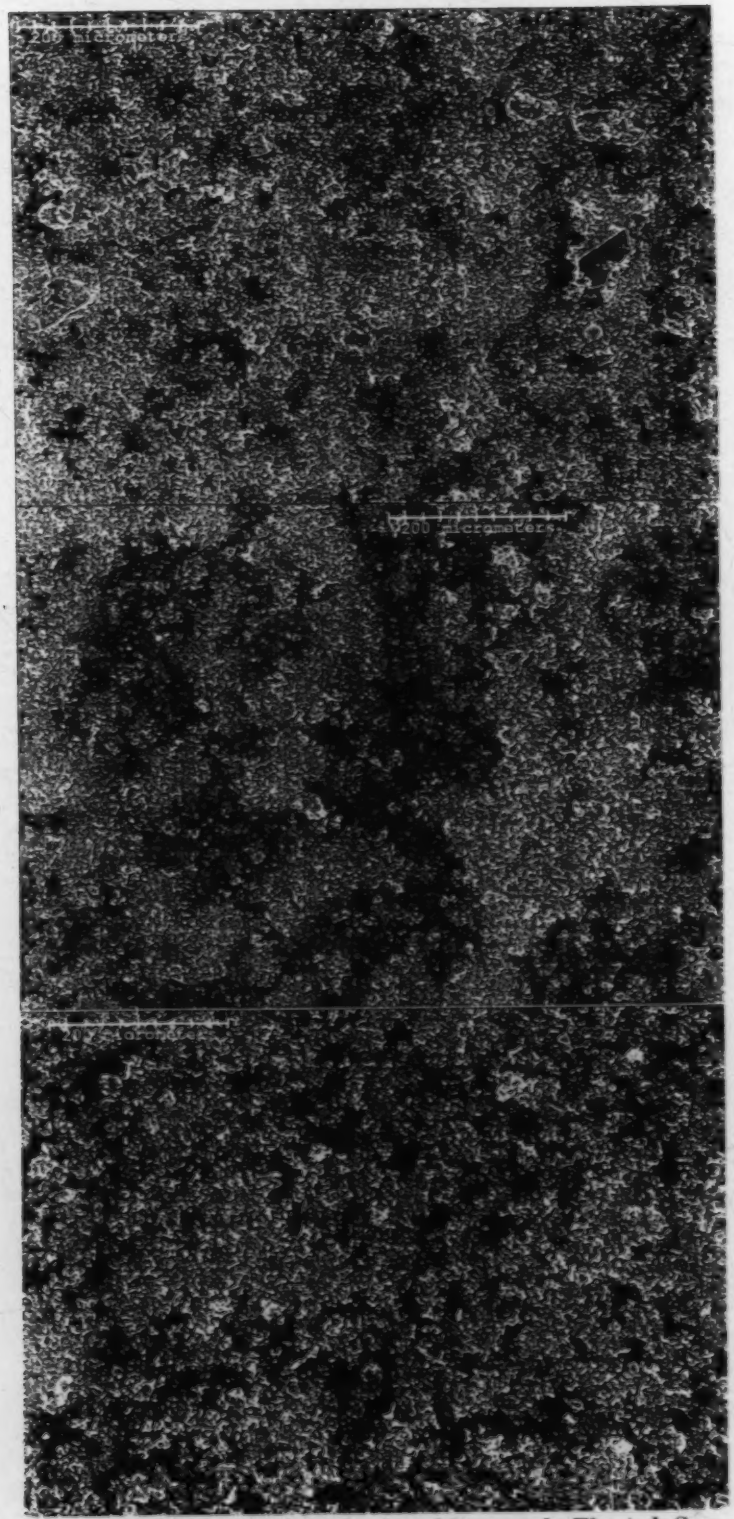
3.2 Roasting Reagents

Food grade salt was used as the source of NaCl throughout this testwork. No difference in vanadium extraction was observed with the use of "free-flowing" table salt (i.e., NaCl with calcium silicate and potassium iodide added), pickling salt (i.e., food grade NaCl with no iodide added) or reagent grade salt.

Other sodium and calcium salts used as additives in the roasting testwork were added as their respective lab grade reagents to the fly ash prior to roasting.

3.3 Precipitation Reagents

Several reagents, including NH_4Cl, $(NH_4)_2S$, H_2SO_4 and $NaClO_3$ were used in the precipitation tests. In all cases, the respective lab grade reagents were used.

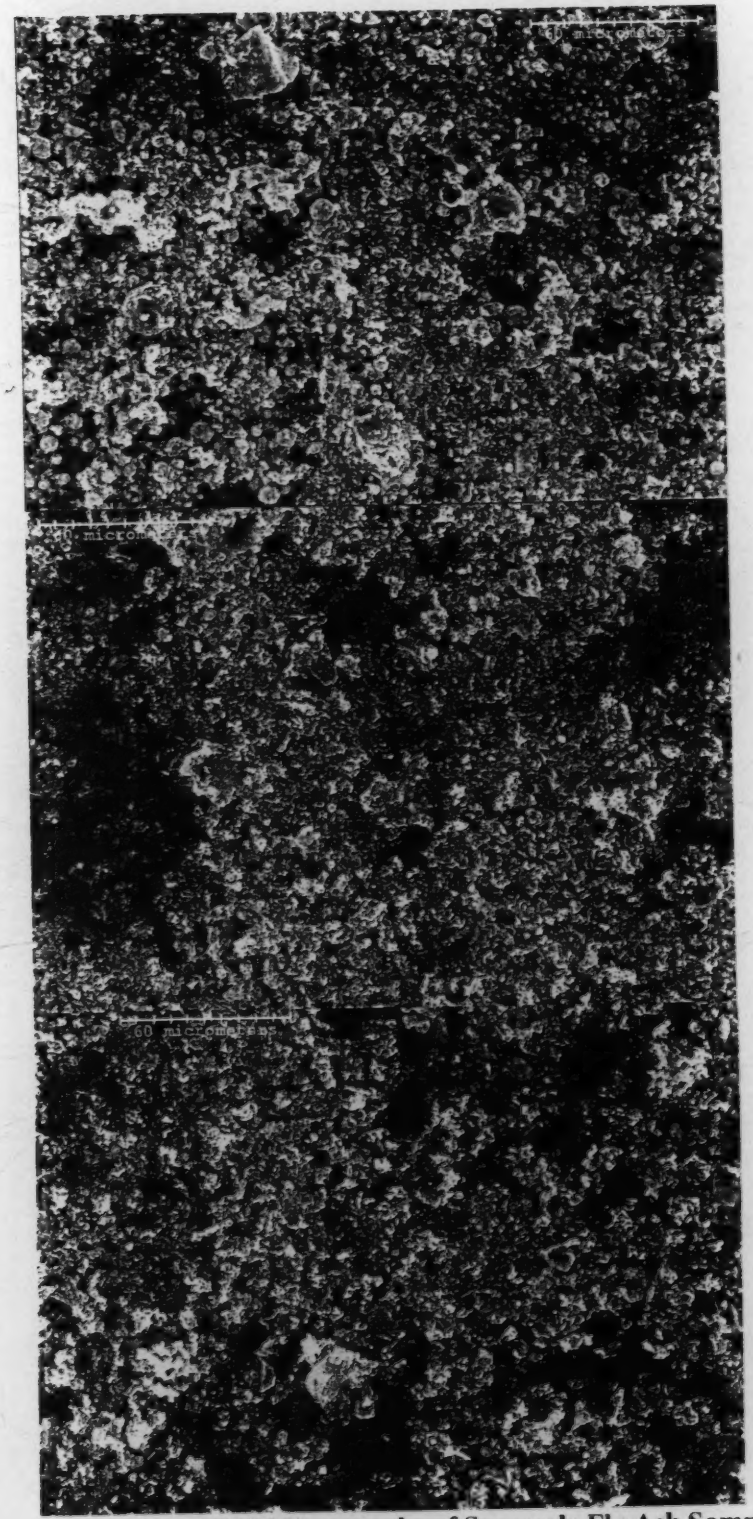


Syncrude Dec 1998
150x Magnification

Syncrude Oct 1998
150x Magnification

Syncrude Jun 2001
150x Magnification

Figure 3.5 SEM Micrographs of Syncrude Fly Ash Samples (150x Magnification)



Syncrude Dec 1998
500x Magnification

Syncrude Oct 1998
500x Magnification

Syncrude Jun 2001
500x Magnification

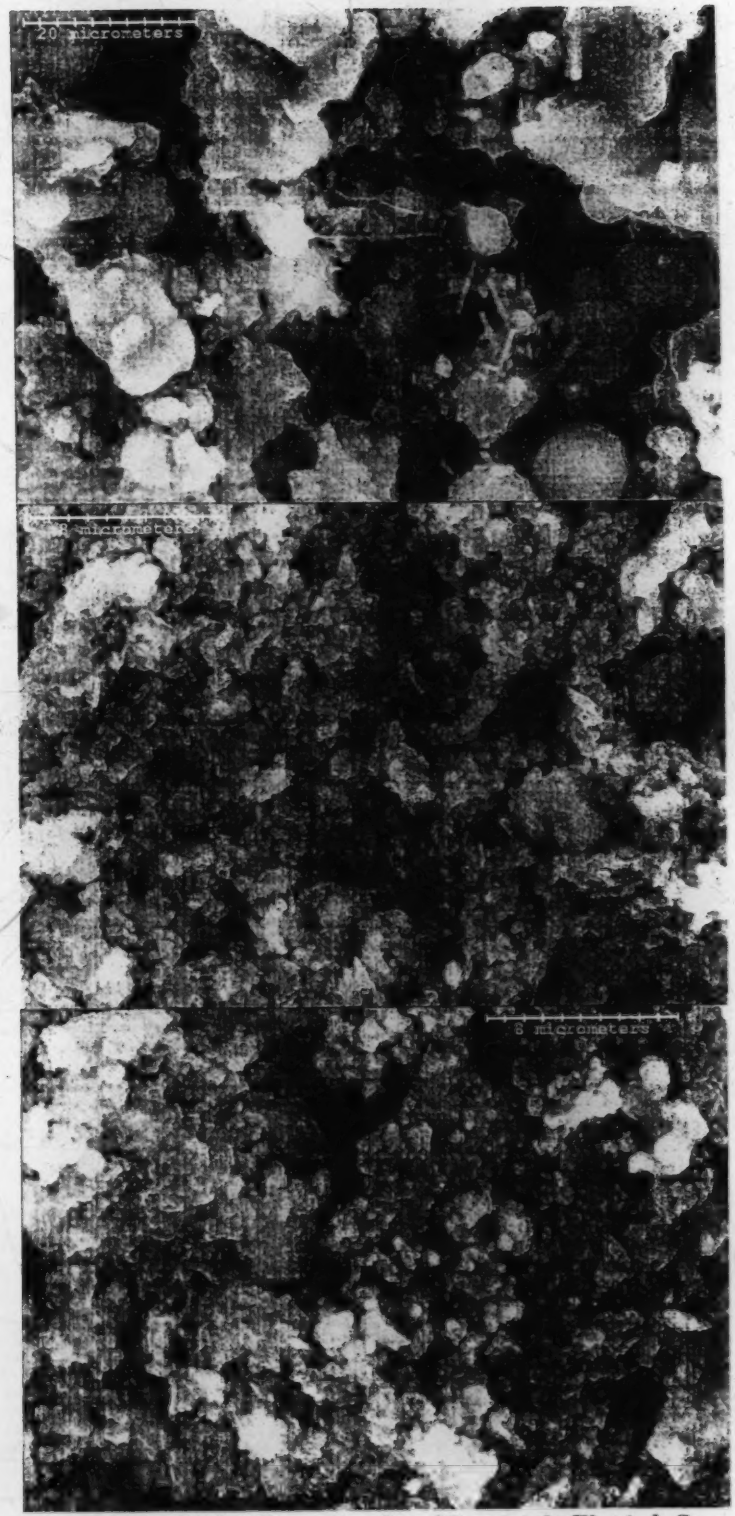
Figure 3.6 SEM Micrographs of Syncrude Fly Ash Samples (500x Magnification)

Syncrude Dec 1998
1500x Magnification

Syncrude Oct 1998
1500x Magnification

Syncrude Jun 2001
1500x Magnification

Figure 3.7 SEM Micrographs of Syncrude Fly Ash Samples (1500x Magnification)



Syncrude Dec 1998
4000x Magnification

Syncrude Oct 1998
4000x Magnification

Syncrude Jun 2001
4000x Magnification

Figure 3.8 SEM Micrographs of Syncrude Fly Ash Samples (4000x Magnification)

4.0 Analysis Methods and Procedure

4.1 Analytical Methods

Most solution analyses were performed using atomic absorption spectroscopy (AA). Routine analyses, including Al, Fe, Mo, Ni, Si, Ti, and V, were made using a single-element Perkin-Elmer 4000 atomic absorption (AA) spectrometer instrument while minor elements were analyzed with a Varian SpectrAA 220FS spectrometer. Sodium and potassium concentrations were measured using a Buck Scientific PFP-7 flame Photometer.

The composition of solid samples was determined by lithium metaborate fusion of the solids, followed by analysis of the resulting solution by atomic absorption spectroscopy. Carbon-free fly ash was required for accurate analysis of the solids, and, thus, samples still containing significant levels of carbon were roasted at 500°C to remove carbon prior to analysis. The ash was fused with lithium metaborate ($LiBO_2$) at 900 to 1000°C, with the fusate dissolved in dilute hydrochloric acid.

In all cases, standards were prepared to minimize matrix effects and interference by other elements in the analyte, based on recommendations given by various atomic absorption manuals (235,236).

4.2 Roasting and Leaching

Decarbonization involved adding as-received fly ash to a porcelain crucible, placing the crucible in a muffle furnace and roasting at 500°C to constant weight. Weights before and after roasting were recorded and are reported as loss on ignition (L.O.I.) in the discussion.

In roasting tests, the preweighed ash was combined with any additives in a mortar and pestle and then transferred to porcelain crucibles. The porcelain crucibles were inserted into the back of a muffle furnace preheated to the desired temperature. (The areas of the muffle furnaces used for roasting showed temperature gradients of 5 to 10°C.) After the

required reaction time, the crucibles were removed and the ash either air-cooled or quenched in water. (For a few tests on Syncrude ash, the roasted ash was quenched into Na_2SO_4 or Na_2CO_3 solutions.)

For roasting large samples of ash for solution purification or precipitation tests, preweighed amounts of ash and salt were combined in a mortar and pestle. This mixture was then transferred with a ladle to a preheated muffle furnace with porous zirconia plates lining the bottom of the furnace. After the required reaction time, the ash was removed from the furnace with a specially designed lifting device and allowed to air cool.

Roasted samples were ground in a mortar and pestle prior to leaching. (Quenched samples were ground as a wet slurry, with the wash and quench solution making up the leach solution while the air cooled samples were pulverized as a dry solid and leached in water.)

Leaching of roasted samples was done in Pyrex beakers using magnetic stir bars and hot plates to provide mixing and heating of the slurry. These tests were carried out at 95 to 97°C for 1 h before filtering the slurry. Filter cakes were washed three times with distilled water, with the volume of the combined filtrate and wash solution measured and a sample of this solution taken for analysis. The filter cake was dried overnight at 95 to 100°C and the weight of the solids recorded. Vanadium extractions from roasting and leaching were generally repeatable within 2 to 3%, and often within 1%.

4.3 Preroast Leaching

Both as-received and decarbonized ash were tested in the preliminary preroast leaching tests. The required weight of solids and volume of the required stock solution were measured and combined in a Pyrex beaker and allowed to mix at 95 to 97°C for 1 h. The samples were then filtered and washed as detailed in Section 4.2.

For the preroast leaching rate tests, larger quantities of solids and solution were added to a larger beaker and allowed to mix at 95 to 97°C. Samples of 25 to 50 mL were then

taken at prescribed time intervals with the samples filtered and washed as detailed in Section 4.2. For the last rate sample, the test was stopped and the remaining slurry was filtered and washed with the same procedure as the other samples.

4.4 Vanadium and Molybdenum Recovery

Large batches of air-cooled, roasted ash were leached with water at 50% solids to produce a concentrated leach solution for the precipitation tests. The slurry was filtered, the filtrate collected, and then the residue was washed to remove any entrained vanadium solution from the solids. The leach solution was then used in various tests to precipitate vanadium as "red cake" or as ammonium metavanadate.

With time, precipitates would begin to form from the concentrated leach solutions. The formation of a distinctly green and a distinctly orange precipitate was observed. Vanadium recovery tests were performed shortly after filtration of the leach liquor to limit the formation of these undesirable precipitates.

4.4.1 Red Cake Precipitation

In the preliminary precipitation tests, the filtrate pH was lowered to between 1 and 2 using 200 g/L H_2SO_4. The filtrate was then heated to 95°C and allowed to react for 1 h. The red vanadium precipitate was filtered and washed with water, adjusted to pH 2 with sulphuric acid, and the combined filtrate and wash solution was analyzed for vanadium. However, the amorphous nature of the vanadium precipitate resulted in partial dissolution of the precipitate during washing so, in future tests, the red cake produced was no longer washed before drying. (The entrained precipitation solutions were found to contribute less than 0.5% impurities to the overall red cake analysis.)

A molybdenum removal process was also developed to remove molybdenum from the leach filtrate prior to precipitation. The filtrate was cooled to 25°C and the pH lowered to pH 1. Reagent grade $(NH_4)_2S$ was added to the filtrate to precipitate molybdenum as a sulphide byproduct. Addition of $(NH_4)_2S$ raised the pH of the solution and, on the lab

scale, several cycles of $(NH_4)_2S$ addition and readjustment of the pH to pH 1 were required to precipitate Mo to low levels. (The solution pH was usually cycled three times between pH 1 and pH 3.) The solution pH was then readjusted to pH 1 to 1.5 to allow filtration of the precipitate formed as the precipitates at pH 3 did not filter readily. The end point of the reaction was noted by the formation of small amounts of H_2S (i.e., gas bubbling at the surface of the solution) and a blue color of the solution, due to the reduction of V^{5+} to V^{4+}. This solution was then filtered, with the filtrate saved and the solids washed to remove entrained solution.

Sodium chlorate was added to oxidize the vanadium in the molybdenum removal solution back to V^{5+}. The solution pH was then lowered to between 1 and 2 using 200 g/L H_2SO_4 and the filtrate was heated to 95°C and allowed to react for 1 h before filtering the slurry. (In some tests, rate samples were taken at intervals between 0.5 and 1.75 h.) The solid sample was dried without washing to eliminate redissolution of vanadium values from the amorphous precipitate.

4.4.2 Ammonium Metavanadate Precipitation

Desilication was performed before vanadium precipitation to lower the silicon in the leach solution and, hence, the silicon in the vanadium product. In desilication, the pH of the leach solution was adjusted to between pH 9 and 11 and the prescribed amount of aluminum sulphate was added to the solution. A pale brown to orange precipitate began to form immediately, but the desilication was allowed to proceed for 30 minutes at 90 to 97°C to digest the precipitate to form a filterable desilication sludge. The slurry was then filtered with the filtrate saved and the solids were washed four times with distilled water.

In ammonium metavanadate precipitation, ammonium chloride was added as a solid to the desilication solution and allowed to react with the solution for 30 minutes at room temperature, before filtering to recover a white ammonium metavanadate product. In one test, a second stage of precipitation was performed on the first stage precipitation solution to improve vanadium precipitation efficiencies. In another test, ammonium sulphide

$(NH_4)_2S$ was added to remove molybdenum from the precipitation solution as a molybdenum sulphide.

4.5 Calculations

Generally, extractions were calculated by two different methods, using the chemical analyses from the solid and solution samples obtained from this testwork. Sample extraction calculations are given below.

$$\text{Extraction (Solids Basis)} = \frac{(\text{Residue Analysis, \%})(\text{Residue Weight, g})}{(\text{Feed Analysis, \%})(\text{Feed Weight, g})} \times 100$$

$$\text{Extraction (Solution Basis)} = \frac{(\text{Solution Analysis, mg/L})(\text{Solution Volume, mL})}{(\text{Feed Analysis, \%})(\text{Feed Weight, g})} \times 100$$

Extractions from roasting and water leaching were calculated using a solids basis; preroast leaching extractions were calculated using a solution basis.

Precipitation efficiencies were calculated using solution analyses and solution volumes, as shown in the calculation below.

$$\text{Precipitation Efficiency} = 100 - \frac{(\text{Final Solution Analysis, mg/L})(\text{Final Volume, mL})}{(\text{Feed Solution Analysis, g/L})(\text{Initial Volume., mL})} \times 100$$

5.0 Preroast Leaching Tests

As discussed in Section 2.4.1, tests on oil sands fly ash indicated that they were not amenable to direct atmospheric leaching. Griffin and Etsell cite vanadium extractions of 17% and 27%, respectively, for 2 N H_2SO_4 (29,185,186) and 3 N NaOH while Gomez-Bueno et al. report extractions of 30% with 2N H_2SO_4 and 60% with 2N NaOH (187,188). Thus, it is unlikely that direct leaching of the ash would be an economical process for recovering vanadium or nickel.

However, in this research, preroast leaching tests were conducted for several reasons:

a) to confirm the leaching results achieved by previous researchers,
b) to characterize and compare the various ash samples,
c) to investigate the oxidation state of the soluble portion of the vanadium in the ash,
d) to determine whether leaching the ash prior to roasting could be used to lower the requirements for sodium salts during salt roasting, and
e) to collect data on the leaching of Syncrude fly ash and decarbonized fly ash.

5.1 Suncor Fly Ash

5.1.1 As-Received Ash

Four lixiviants were tested on the as-received Suncor fly ash: water, Na_2CO_3 (100 g/L), NaOH (100 g/L), and H_2SO_4 (178 g/L). Figure 5.1 shows the vanadium extractions from these tests.

The highest vanadium extractions, for a given sample, were accomplished by leaching with sulphuric acid, with vanadium extractions for the various ash samples ranging from 18 to 56%. Less than 9%, and generally less than 2%, vanadium extraction was possible using water as a lixiviant. Leaching with Na_2CO_3 resulted in extractions of between 6 and 20% while NaOH leached 31 to 51% of the vanadium from the samples tested. Thus in general, the four lixiviants tested produced difference ranges of vanadium extraction and this allows the reagents to be ranked by increasing severity (water<Na_2CO_3<NaOH<H_2SO_4).

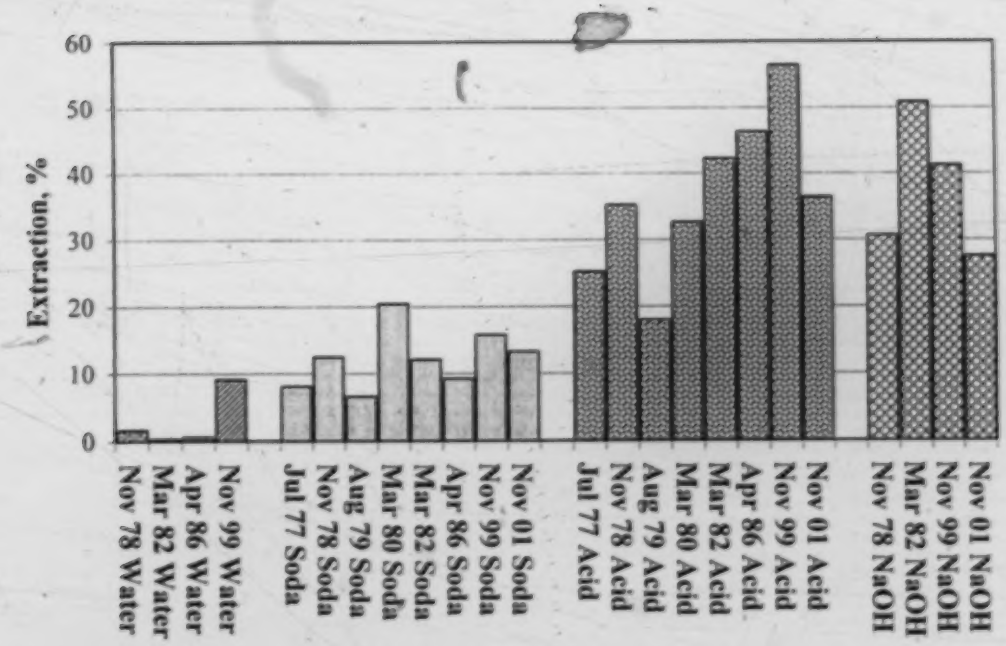


Figure 5.1 Vanadium Extractions from Leaching As-Received Suncor Fly Ash

Vanadium is believed to be present as V^{5+} in the water, Na_2CO_3 or NaOH leach solutions because the characteristic yellow color of the VO_2^+ ion was observed when those solutions were acidified.

However, the solutions produced by leaching with sulphuric acid were either green (samples produced after 1982) or blue (samples produced before 1982) in color. Initially, it was believed that the green color represented the formation of V^{3+} (green), but, on analysis, the green color was shown to be due to the presence of the Fe^{3+} ion (2.5 g/L); solutions with lower levels of iron were blue in color. Titration with potassium permanganate indicated that the vanadium in both the blue and green acidic leach solutions was present as V^{4+}.

The formation of V^{4+} in the acidic leach solutions is believed to be caused by reduction of V^{5+} with carbon from the fly ash in acid solution, as shown in the half reactions overleaf (237).

Oxidation: $C + 2\ H_2O \rightarrow CO_2 + 4\ H^+ + 4\ e^-$
Reduction: $4\ V^{5+} + 4\ e^- \rightarrow 4\ V^{4+}$

Vanadium was present as V^{4+} in all samples of as-received ash leached in acidic solution, but not in basic or neutral leach solutions, indicating that the carbon only acts as a reducing agent at lower pH. Since leaching with both NaOH and H_2SO_4 gave similar ranges of vanadium extraction, it is likely that all of the leachable vanadium is present in the fly ash as V^{5+}.

The following table shows the range of extractions for several major impurities during leaching of the as-received Suncor fly ash.

Table 5.1 Dissolution of Impurities in Leaching of As-Received Suncor Ash

Lixiviant	Water		Na_2CO_3		H_2SO_4		NaOH	
Extraction, %	Min	Max	Min	Max	Min	Max	Min	Max
V	0.3	9.1	6.5	20.4	18.0	56.4	27.5	50.8
Al	0.0	1.2	0.2	3.0	4.3	18.1	0.8	3.4
Fe	0.0	0.1	0.0	0.1	8.9	22.8	0.0	0.1
Mo	1.7	6.0	19.5	>99.9	25.6	68.1	26.5	71.8
Ni	0.1	6.3	0.0	0.3	9.1	23.3	0.0	0.9
Si	0.0	0.2	0.0	0.2	0.1	1.1	7.3	13.7
Ti	0.0	0.1	0.0	0.2	0.5	18.2	0.0	0.0

In all these tests, the extraction of molybdenum from the ash was similar or slightly higher than the extraction of vanadium. The solution chemistry of molybdenum is very similar to that of vanadium and, for the most part, conditions or lixiviants that improve vanadium extraction would be expected to improve molybdenum extraction.

Water and sodium carbonate leach vanadium and molybdenum selectively from the ash with minimal dissolution of the other impurities, but also resulted in very low vanadium extractions (<21%). The other two lixiviants produced higher vanadium extractions, but resulted in significant dissolution of several impurities. Sulphuric acid dissolved elements with higher solubilities in acidic solution (Al, Fe, Ni and Ti) while sodium

hydroxide dissolved high levels of elements soluble in very basic solutions (Si). Thus, neither of two lixiviants was selective to vanadium or molybdenum.

5.1.2 Carbon-Free Ash

Similar leach tests were conducted on selected samples of Suncor fly ash after the carbon in the ash had been removed by roasting at 500°C. The vanadium extractions are shown in the following figure.

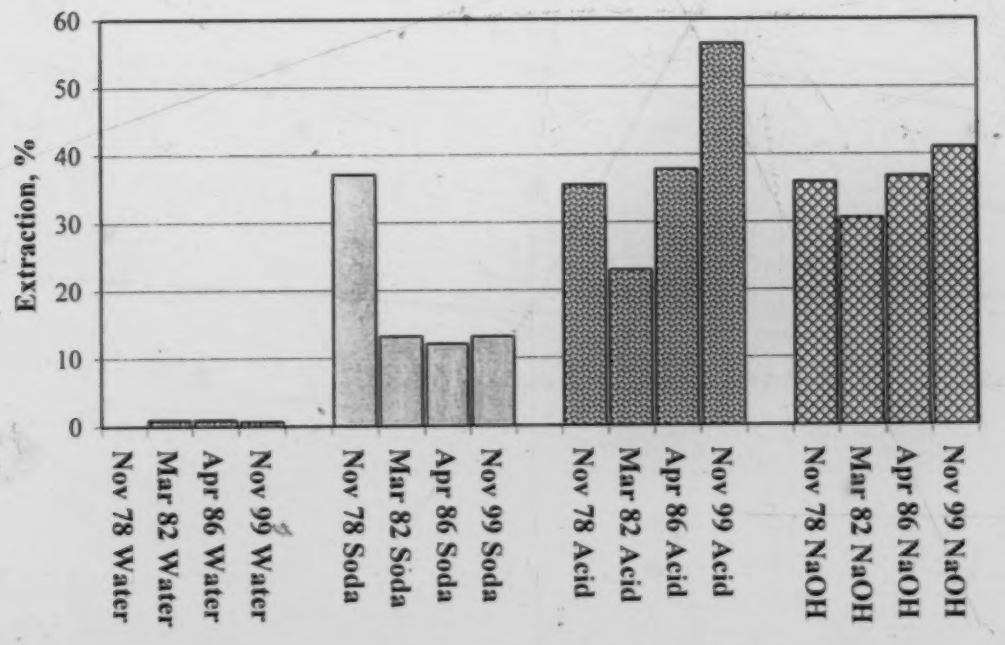


Figure 5.2 Vanadium Extractions from Leaching Carbon-Free Suncor Fly Ash

For the most part, the vanadium extractions from leaching the decarbonized ash are similar or lower than those from leaching the as-received ash; less variability in the extractions from sample to sample for the basic and neutral lixiviants are observed. (The Nov 78 ash is an exception as a high extraction was achieved when leaching with sodium carbonate and the extraction did not increase with the use of more aggressive lixiviants.) The same conclusions on the relative severity of the lixiviants (water<Na_2CO_3<NaOH<H_2SO_4) can be drawn from these tests, but the difference

between the extractions from NaOH and H_2SO_4 are less pronounced than from the as-received ash.

In all of the leaching tests on decarbonized ash, the solutions were yellow, or turned yellow on acidification, indicating that the vanadium in the leach solutions was present as VO_2^+ (V as V^{5+}).

The following table shows the range of extractions for the major impurities during leaching of the decarbonized Suncor fly ash.

Table 5.2 Dissolution of Impurities in Leaching of Decarbonized Suncor Ash

Lixiviant	Water		Na_2CO_3		H_2SO_4		NaOH	
Extraction, %	Min	Max	Min	Max	Min	Max	Min	Max
V	0.0	0.9	12.1	37.1	22.9	56.3	30.6	41.1
Al	0.0	1.4	0.1	0.4	0.9	14.0	0.2	1.7
Fe	0.0	0.1	0.0	0.1	2.4	24.3	0.0	0.0
Mo	0.1	6.0	29.8	75.2	25.7	58.3	28.2	61.6
Ni	0.0	1.0	0.0	0.0	5.2	23.3	0.0	0.1
Si	0.0	0.2	0.0	0.0	0.1	0.1	10.2	13.2
Ti	0.0	0.0	0.0	0.0	1.3	7.9	0.0	0.1

Similar ranges of the major impurities dissolved from the decarbonized ash and the as-received ash. Molybdenum, as before, is leached to a similar or slightly higher degree than vanadium and similar groups of impurities were leached with acid (i.e., Al, Fe, Ni and Ti) and NaOH (i.e., Si) as were leached from the as-received fly ash.

5.2 Syncrude Fly Ash

5.2.1 As-Received Ash

The same four lixiviants (water, Na_2CO_3, H_2SO_4, and NaOH) were tested on the three available samples of Syncrude fly ash. The figure overleaf shows the vanadium extractions from those leaching tests.

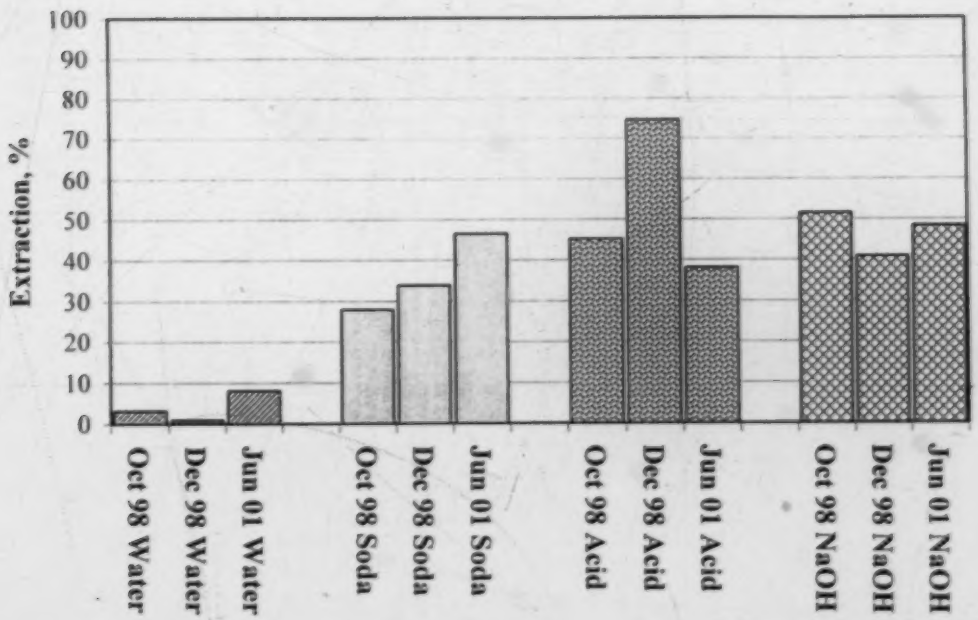


Figure 5.3 Vanadium Extractions from Leaching As-Received Syncrude Fly Ash

The water extractions were of similar magnitude to those from the Suncor ash, but, for all the other lixiviants, the vanadium extractions were generally higher than those achieved from the Suncor ash under the same leaching conditions. Leaching the Syncrude ash with Na_2CO_3 and H_2SO_4 showed the greatest difference from the Suncor ash with the maximum extractions reaching as high as 46 and 75%, respectively. (Maximum extractions were 20 and 56% from Suncor ash for Na_2CO_3 and H_2SO_4, respectively.) Leaching with NaOH produced the same maximum extraction as with Suncor fly ash, but the minimum extraction was 40%, indicating that there was a tighter range of extractions with NaOH for the Syncrude ash. In general, the Syncrude samples tested generally showed a narrower range of extractions than observed for the Suncor ash.

Figure 5.4 shows the range of extractions for the major impurities during leaching of the as-received Syncrude fly ash.

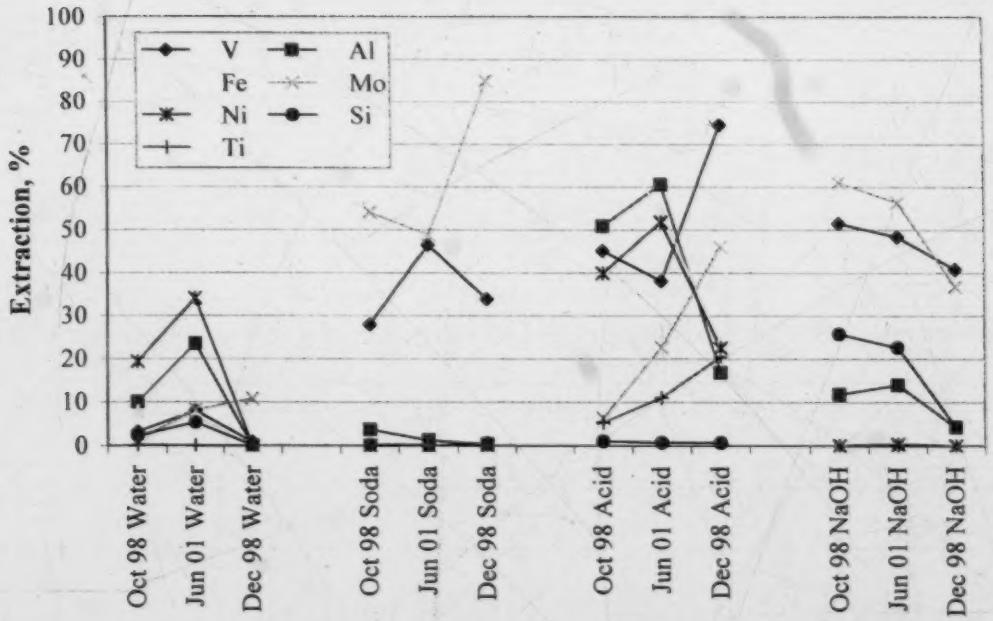


Figure 5.4 Impurity Dissolution from Leaching As-Received Suncor Fly Ash

Much higher levels of impurities were dissolved from the Oct 98 and Jun 01 ash samples than from the Dec 98 sample. (Leaching with Na_2CO_3 is an exception as few impurities, except Mo, were dissolved from all of the samples tested.) Most elements analyzed, including Al, Fe, Mo, Ni and Si, were partially soluble, even in water, from the Oct 98 and 2001 ash samples. Acid leaching resulted in high extractions of Al, Fe and Ni and, high levels of Al and Si were dissolved during NaOH leaching, giving Al:V and Si:V ratios of 0.5:1 to 3:1 in the NaOH leach solutions.

However, the Dec 98 ash behaved similarly to the Suncor ash (Table 5.3). Similar levels of impurities were dissolved with each of the four lixiviants, with water and Na_2CO_3 being essentially selective to V and Mo, with Al and Si being dissolved with NaOH, and with significant dissolution of Al, Fe, Mo, Ni and Ti during acid leaching.

Table 5.3 Comparison of the Dissolution of Impurities from Leaching Syncrude Dec 98 and Suncor Ashes

Lixiviant	Water		Soda		Acid		NaOH	
Extraction, %	Suncor (Max)	Dec 98	Suncor (Max)	Dec 98	Suncor (Max)	Dec 98	Suncor (Max)	Dec 98
V	0.9	0.9	37.1	33.8	56.3	74.5	41.1	40.8
Al	1.4	0.0	0.4	0.3	14.0	16.8	1.7	4.3
Fe	0.1	0.0	0.1	0.0	24.3	23.7	0.0	0.1
Mo	6.0	10.8	75.2	85.0	58.3	46.1	61.6	36.7
Ni	1.0	0.1	0.0	0.0	23.3	22.5	0.1	0.0
Si	0.2	0.1	0.0	0.5	0.1	0.7	13.2	4.4
Ti	0.0	0.0	0.0	0.1	7.9	20.5	0.1	0.0

Some of the differences between the behaviour of the three Syncrude ash samples can be explained by looking at the structures of the ash samples with the scanning electron microscope (SEM) (Section 3.1.2.2). The presence of microcrystals in the Dec 98 ash could explain why more vanadium could be leached from the Syncrude ash than the Suncor ash before salt roasting as microcrystals have been linked to vanadium solubility. (185) The presence of cenospheres in the Dec 98 ash, but their absence from the other Syncrude ash samples, may indicate that the Dec 98 was formed at higher operating temperatures than the other Syncrude ash samples as cenosphere formation is generally linked with high temperature boiler operations (23). The pattern of impurity dissolution and significant proportion of poorly crystalline material, as shown by the multitude of broad peaks in the XRD pattern, in the Dec 98 ash are also similar to those for the Suncor ash, thus adding further support for this hypothesis.

The leach solutions were blue (V^{4+}) for acid leach solutions and were generally clear for basic and neutral leach solutions. (The neutral and basic solutions turned yellow, indicating the presence of vanadium as V^{5+}, when the pH was lowered.) As expected, the carbon in the as-received Syncrude ash reacted with the vanadium in the acidic leach solution to reduce it from V^{5+} to V^{4+}, which is similar to the behaviour observed when the as-received Suncor ash was leached (Section 5.1.1).

5.2.2 Carbon-Free Ash

A limited number of tests were also conducted on carbon-free Syncrude ash. The vanadium extractions from these tests are shown in Figure 5.5.

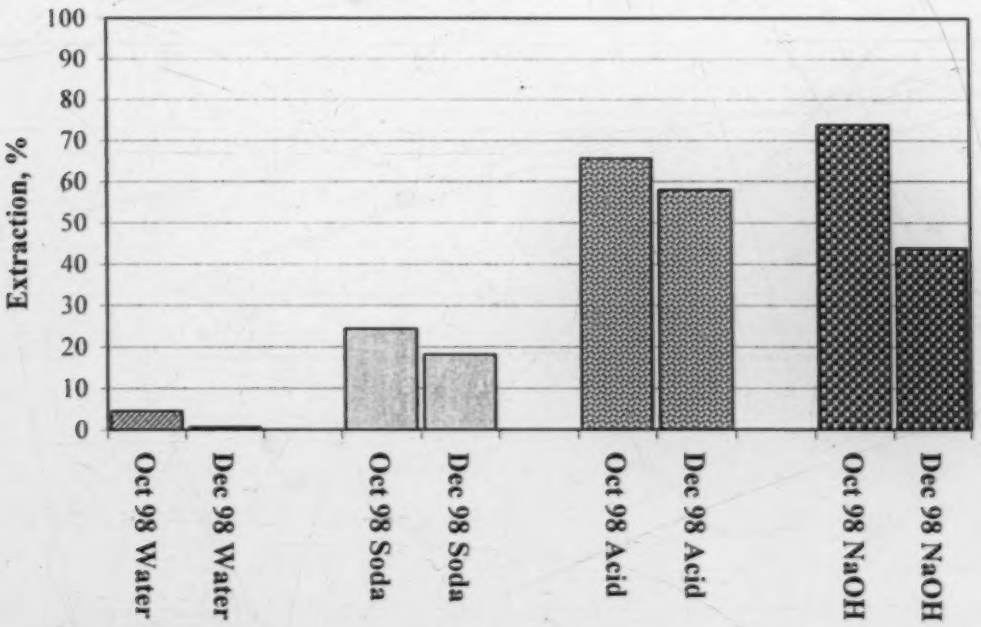


Figure 5.5 Vanadium Extractions from Leaching Carbon-Free Syncrude Fly Ash

The Dec 98 sample of ash behaved similarly to the decarbonized Suncor. For the most part, the vanadium extractions from leaching the decarbonized ash are similar or lower than those from leaching the as-received ash and the same general conclusion on the relative severity of the lixiviants (water<Na_2CO_3<NaOH<H_2SO_4) is observed for the Dec 98 ash.

On the other hand, the Oct 98 ash sample gave roughly 20% higher extractions upon leaching with sulphuric acid or sodium hydroxide when the carbon was removed. As well, the highest extraction was achieved when leaching with NaOH, rather than with H_2SO_4, as in the all the other tests discussed in this section. It is possible that changes to the structure or mineralogy of the Oct 98 ash during roasting at 500°C may be the cause

of this behaviour as the Oct 98 ash may be more sensitive to the temperature of decarbonization as it is believed to have formed at lower temperatures than the Dec 98 or Suncor ashes.

In all of the leaching tests on decarbonized ash, the solutions were yellow, or turned yellow on acidification, indicating that the vanadium in the leach solutions was present as VO_2^+ (V as V^{5+}).

The dissolution of major impurities during leaching of the decarbonized ash is shown in Table 5.4. For the Dec 98 ash, leaching with water, Na_2CO_3 and H_2SO_4 generally resulted in lower levels of dissolved impurities than were dissolved from the as-received ash; the amount of impurities leached with NaOH was virtually unchanged from the as-received ash. The concentration of impurities was also lower for the Oct 98 ash sample, with the exception of certain elements for each reagent which dissolved to higher levels (i.e. Ni (water), Al (Na_2CO_3) and Mo (H_2SO_4)).

Table 5.4 Dissolution of Impurities in Leaching of Decarbonized Syncrude Ash

Lixiviant	Water		Soda		Acid		NaOH	
Extraction, %	Oct 98	Dec 98	Oct 98	Dec 98	Oct 98	Dec 98	Oct 98	Dec 98
V	4.5	0.6	24.3	18.1	65.5	58.0	73.7	43.8
Al	0.4	0.0	15.9	0.2	23.3	5.4	10.6	1.7
Fe	0.3	0.0	0.0	0.0	19.6	14.4	0.1	0.0
Mo	1.7	2.8	58.0	77.4	42.9	43.2	39.2	41.1
Ni	55.9	3.7	0.0	0.0	49.3	26.4	0.1	0.0
Si	0.5	0.0	0.0	0.0	0.9	0.1	13.2	5.8
Ti	0.1	0.1	0.0	0.0	1.5	7.7	0.0	0.0

5.3 Rate Tests

Several tests were also conducted to determine whether higher vanadium extractions could be achieved with longer leaching times. Suncor ash from 1986 and Syncrude ash from Dec 98 were tested both before and after roasting to remove carbon. The results from these tests are shown in Figures 5.6 to 5.9. The leaching results from Section 5.1 after leaching for 1 h are plotted for comparison.

For the most part, very little additional vanadium can be extracted from either the as-received or decarbonized Suncor ash. Leaching decarbonized Suncor ash with NaOH was the one exception, as the vanadium extraction can be improved from 30 to 60% by increasing the leaching time from 1 to 2 h.

Leaching the Syncrude Dec 98 ash for longer times gave modest improvements in the vanadium extraction. Increases in the extraction of 4, 13 and 12% for Na_2CO_3, H_2SO_4 and NaOH, respectively, were possible for the as-received ash. The vanadium extraction was improved by 9 and 26% for H_2SO_4 and NaOH, respectively, for the decarbonized ash, with no increase in the extraction from Na_2CO_3 observed.

Overall, even with extending the leaching times, vanadium extractions were still generally low, with higher extractions associated with large increases in the dissolution of impurities, such as Al, Si and Fe.

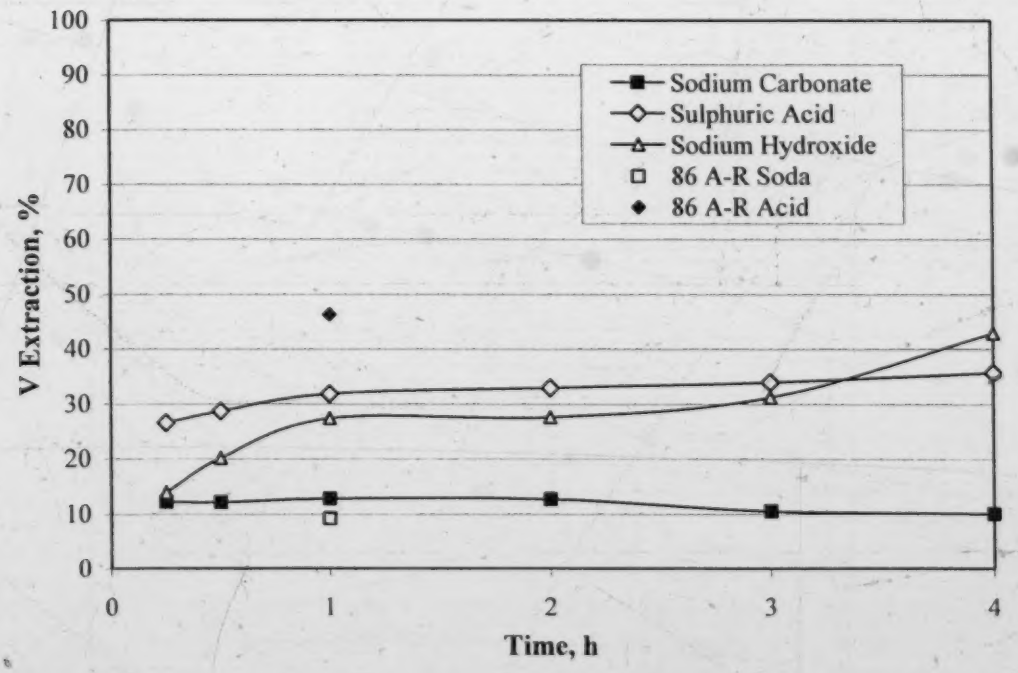


Figure 5.6 Leaching Rate Tests on As-Received Suncor 1986 Ash

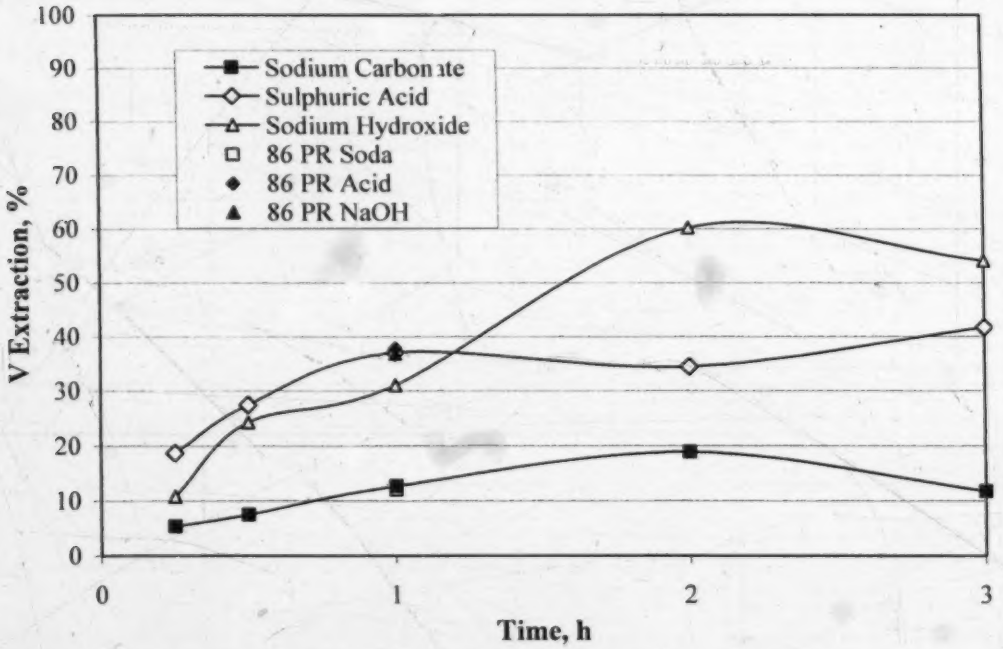


Figure 5.7 Leaching Rate Tests on Decarbonized Suncor 1986 Ash

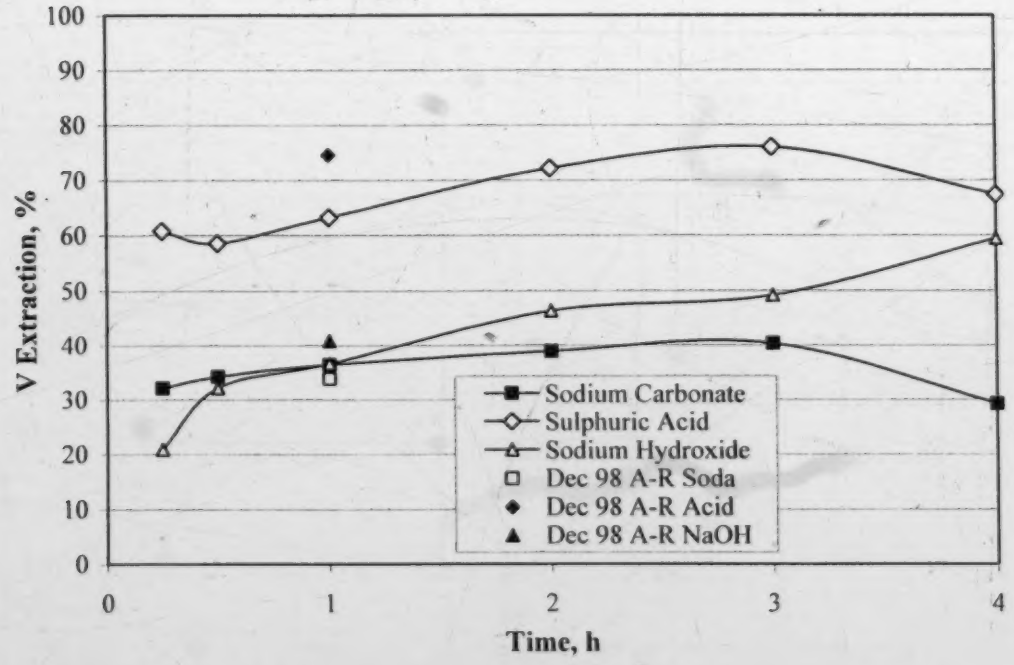


Figure 5.8 Leaching Rate Tests on As-Received Syncrude Dec 98 Ash

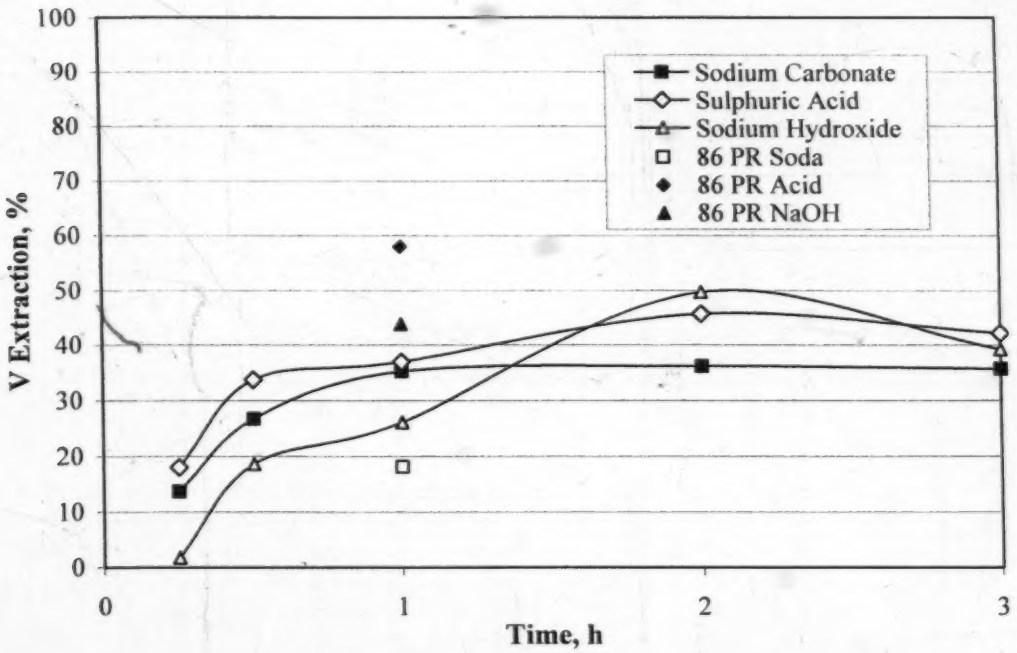


Figure 5.9 Leaching Rate Tests on Decarbonized Syncrude Dec 98 Ash

5.4 Leaching Prior to Salt Roasting

Three tests were performed to determine whether the prior removal of soluble vanadium from oil sands fly ash would lower the requirements for salt addition during salt roasting. Samples of Suncor 1982 ash leached with H_2SO_4 or NaOH were roasted with 15 or 25% NaCl at 850°C for 4 h. Overall extractions of only 44 to 71% were achieved; the vanadium extractions were significantly lower than the 75 to 85% extractions typically achieved by roasting the Suncor 1982 ash without prior leaching. The presence of aluminum and silicon in the ash may explain this behaviour, as much of the salt added in roasting has been found to react with the aluminosilicate fraction of ash (Section 6) and, thus, only minor reductions in NaCl addition may be possible.

5.5 Conclusions

Leaching tests were conducted on several fly ash samples, both before and after roasting at 500°C to remove carbon, and typical vanadium extractions from these tests are summarized in the table below.

Lixiviant	Suncor		Syncrude	
	As-Received	Decarbonized	As-Received	Decarbonized
Water	0-9%	0-1%	5-11%	1-5%
Na_2CO_3 (100 g/L)	6-20%	12-37%	28-46%	18-24%
NaOH (100 g/L)	27-51%	31-41%	41-51%	44-74%
H_2SO_4 (178 g/L)	18-56%	23-56%	38-75%	58-66%

From these tests, several observations can be made. First, different reagents produced difference ranges of vanadium extractions and this allows the reagents to be ranked by increasing severity (water<Na_2CO_3<NaOH<H_2SO_4). Water and Na_2CO_3 were selective to vanadium, but only low vanadium extractions were possible with these reagents. Leaching with NaOH and H_2SO_4 gave higher extractions, but also dissolved significant amounts of Si (NaOH) or Al, Fe, Ni and Ti (H_2SO_4), in addition to vanadium. Second, the range of extractions for a given reagent is quite wide, indicating significant variation in the leaching behaviour of the various ash samples. Third, for all the Suncor ashes and one Syncrude ash, leaching of pre-roasted ash generally resulted in lower vanadium extractions, compared with leaching the as-received ash for a given sample. Fourth, vanadium extractions were generally higher from Syncrude fly ash than from Suncor fly ash and much more variation, especially in the solubility of many impurities, was seen in the Syncrude ash samples that were tested. Finally, the overall vanadium extractions from atmospheric leaching were quite low, even with the harshest reagent tested and with longer leaching times, and the best extractions can only be achieved with poor selectivity to vanadium. Thus, atmospheric leaching of the Suncor and Syncrude fly ash would likely not be feasible for commercial production of vanadium from these materials.

Based on the results of these tests, the leachable vanadium, which ranges between 40 and 70% of the total vanadium, is believed to be present in the fly ash entirely as V^{5+}.

6.0 Salt Roasting of Suncor Fly Ash

With the prospect of producing vanadium commercially from fly ash, an understanding of the variability of the fly ash with time is an important operating consideration as a consistent feed source, with a consistent roasting behaviour, would be important for any commercial operation.

Thus, a series of tests was conducted to determine the response of the eight available samples of Suncor fly ash to the three major salt roasting parameters: salt addition, time and temperature. Roasting tests with no salt added were also conducted on one ash sample for comparison.

6.1 Fly Ash Composition

The chemical compositions of samples from 1977 to 2001 are shown in Table 5.1. Some variability in the vanadium concentration occurs from sample to sample with a range of vanadium grade of 2.5 to 3.6%, but, overall, the composition of the ash fraction of the fly ash is quite consistent, with the only major variations being in the carbon content of the fly ash. Based on the carbon content of the other available fly ash samples, the 1980 sample likely represents an upset condition in the Suncor boilers as the carbon content was much higher than any of the other Suncor ash samples. Calcium is the only other major element analyzed that varied significantly from sample to sample (0.77 to 1.77%).

Table 6.1 Suncor Fly Ash Analyses, wt%

Date	V	Al	Ca	Fe	Mo	Ni	Si	Ti	L.O.I.
1977	3.02	12.2	1.11	5.33	0.17	1.00	22.8	2.02	58.6
1978	3.02	11.2	1.77	4.41	0.17	0.95	25.0	1.72	62.0
1979	2.49	13.0	0.86	3.66	0.11	0.82	23.0	1.84	35.4
1980	3.63	12.1	0.77	3.83	0.28	1.05	27.2	1.89	88.4
1982	3.58	12.7	0.80	5.63	0.23	1.12	26.2	1.65	27.3
1986	3.19	13.1	1.18	5.65	0.18	1.01	26.4	1.46	26.7
1999	3.02	11.0	1.27	5.49	0.19	0.97	25.2	1.62	58.9
2001	2.86	10.7	1.67	5.11	0.20	0.92	28.4	1.43	23.1

6.2 Roasting Tests

6.2.1 Roasting with No Additives

The vanadium extractions for 1982 fly ash roasted with no additives at various temperatures and then water leached is shown in Figure 6.1.

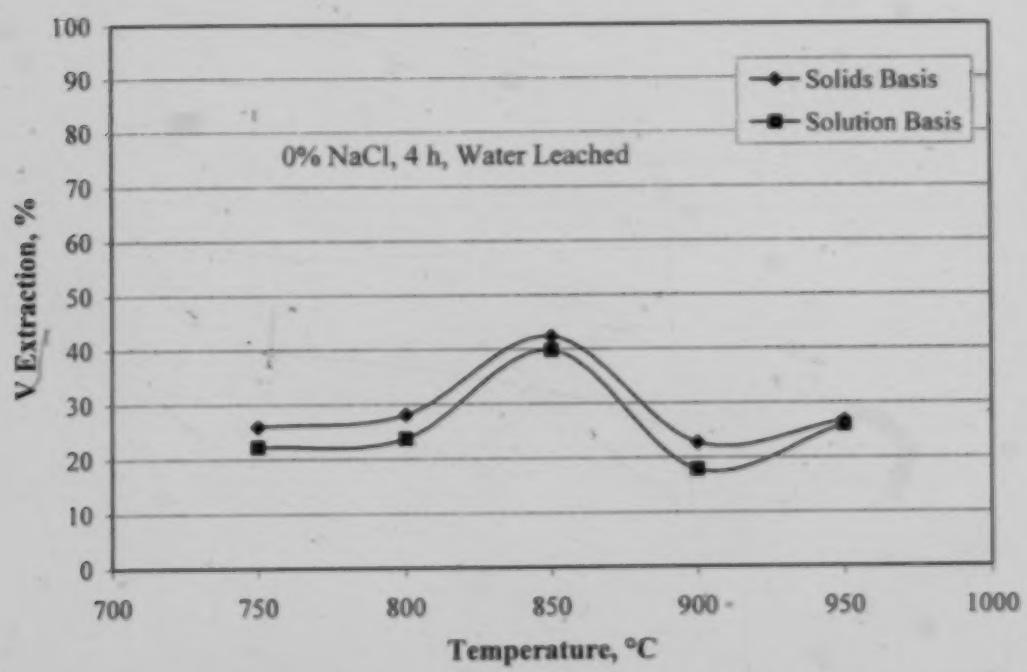


Figure 6.1 Effect of Temperature on Roasting of Suncor 1982 Fly Ash Without Roasting Additives

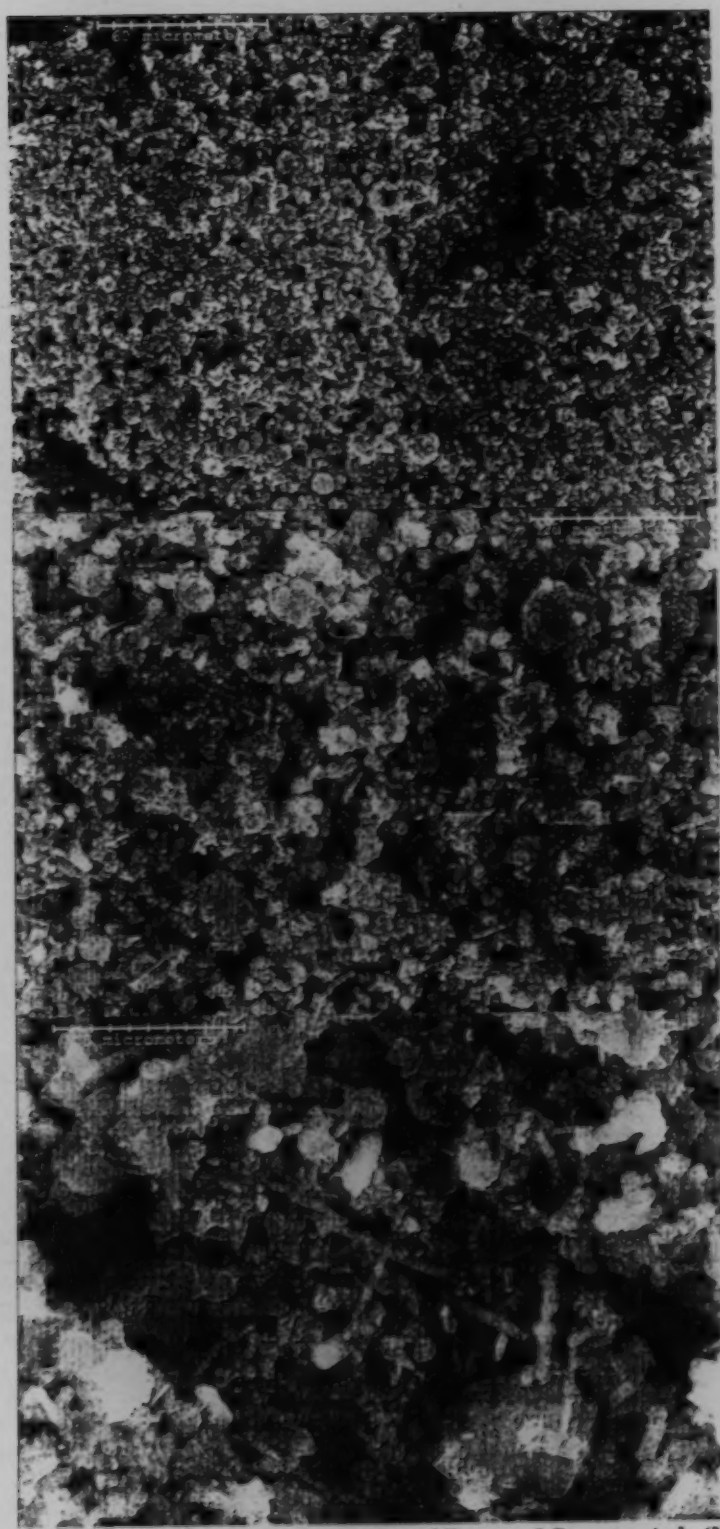
The vanadium extractions for roasting without any reagents are considerably higher than the extractions achieved by directly leaching the decarbonized Suncor fly ash with water (i.e. extractions of less than 1% (Section 5.1.2)). The maximum extraction is achieved at 850°C, with the extractions above and below that temperature ranging from 23 to 28%.

As seen in Figure 6.2, SEM micrography shows that, after heating at 850°C for 4 h, the majority of the cenospheres in the as-received ash have decomposed on heating to form an aluminosilicate matrix and fine elongate crystals enriched in iron and titanium. Instead of the poorly crystalline XRD pattern of the as-received ash, the ash heated at 850°C shows a definite pattern of x-ray diffraction peaks (Figure 6.3). The presence of

$Na_2Al_{2x}O_{3x+1}$, an orthorhombic compound with a mullite-type structure, cristobalite, a high temperature polymorph of SiO_2, and pseudobrookite (Fe_2TiO_5) were identified from the XRD pattern for this sample.

At first consideration, the formation of mullite-type compounds and cristobalite seems unreasonable as these compounds are generally known to form at very high temperatures (i.e., between 1100 and 1400°C) (234). However, recent studies into the reactions that occur during firing of V-doped clay bricks indicate that both compounds can form at much lower temperatures in the presence of vanadium (234,238). Figure 6.3 shows the reaction sequences observed in clays with and without the addition of vanadium. All of the samples from those tests were held for long times (i.e., 17 h) at the desired temperature to determine the equilibrium phases that would be present in that system. It is suspected, however, that the relatively short retention time of the fly ash in Suncor's boilers, and the fast cooling of the ash, did not allow sufficient time for mullite, cristobalite or pseudobrookite to form and, thus, produced an ash containing a much higher proportion of amorphous, or poorly crystalline, material than reported in the work by Bruhns et al.

The phases formed on subsequent heating of the Suncor ash, however, are in good agreement with the equilibrium phases reported by Bruhns et al. The limited vanadium solubility may indicate that, though some of the vanadium in the fly ash is converted to water-soluble vanadium compounds, most of the vanadium becomes incorporated in other phases present in the ash. (In both this work and the testwork by Bruhns et al., roughly 30% of the vanadium in the ash became water soluble on roasting.) From the work by Bruhns et al, there no indication that vanadium is incorporated into the cristobalite structure and, to date, no evidence of vanadium in the pseudobrookite structure has been found, even during simulations of similar conditions in a TiO_2-Fe_2O_3-V_2O_5 system (234). Another paper by the same group of researchers indicates that the mullite structure can accommodate up to 5.7 wt% V (239). Thus, it is likely that the majority of the residual vanadium is associated with the mullite-type phase $Na_2Al_{2x}O_{3x+1}$, where it is suspected that V and Si partially substitute for tetrahedral Al in that structure.



Suncor 1982 –0% NaCl
500x Magnification

Suncor 1982 –0% NaCl
1500x Magnification

Suncor 1982 –0% NaCl
4000x Magnification

Figure 6.2 SEM Micrographs of Roasted Suncor Ash (No Additives, Quenched)

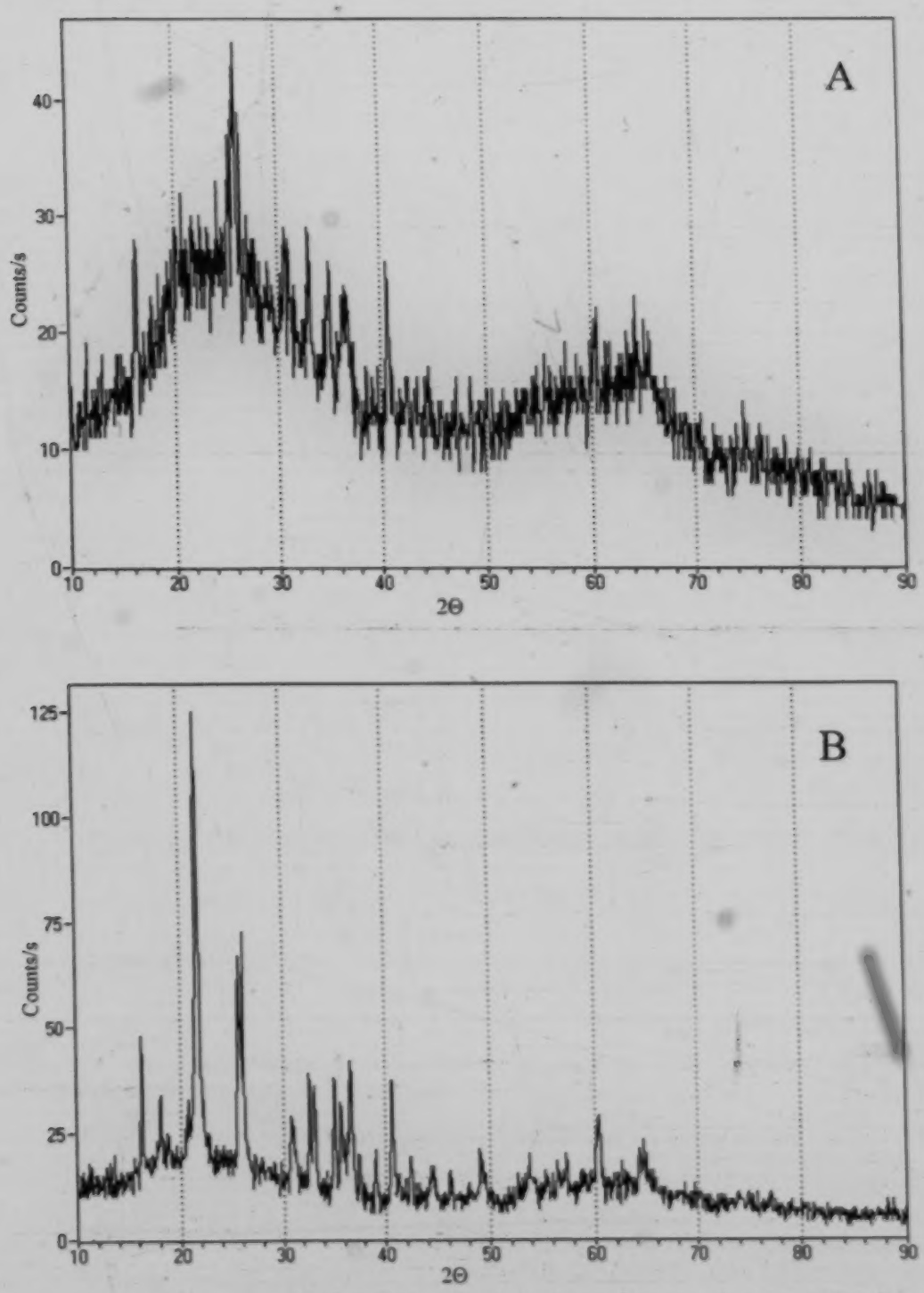


Figure 6.3 X-Ray Diffraction Patterns: a) As-Received Suncor Fly Ash, and b) Suncor Fly Ash Roasted with No Additives

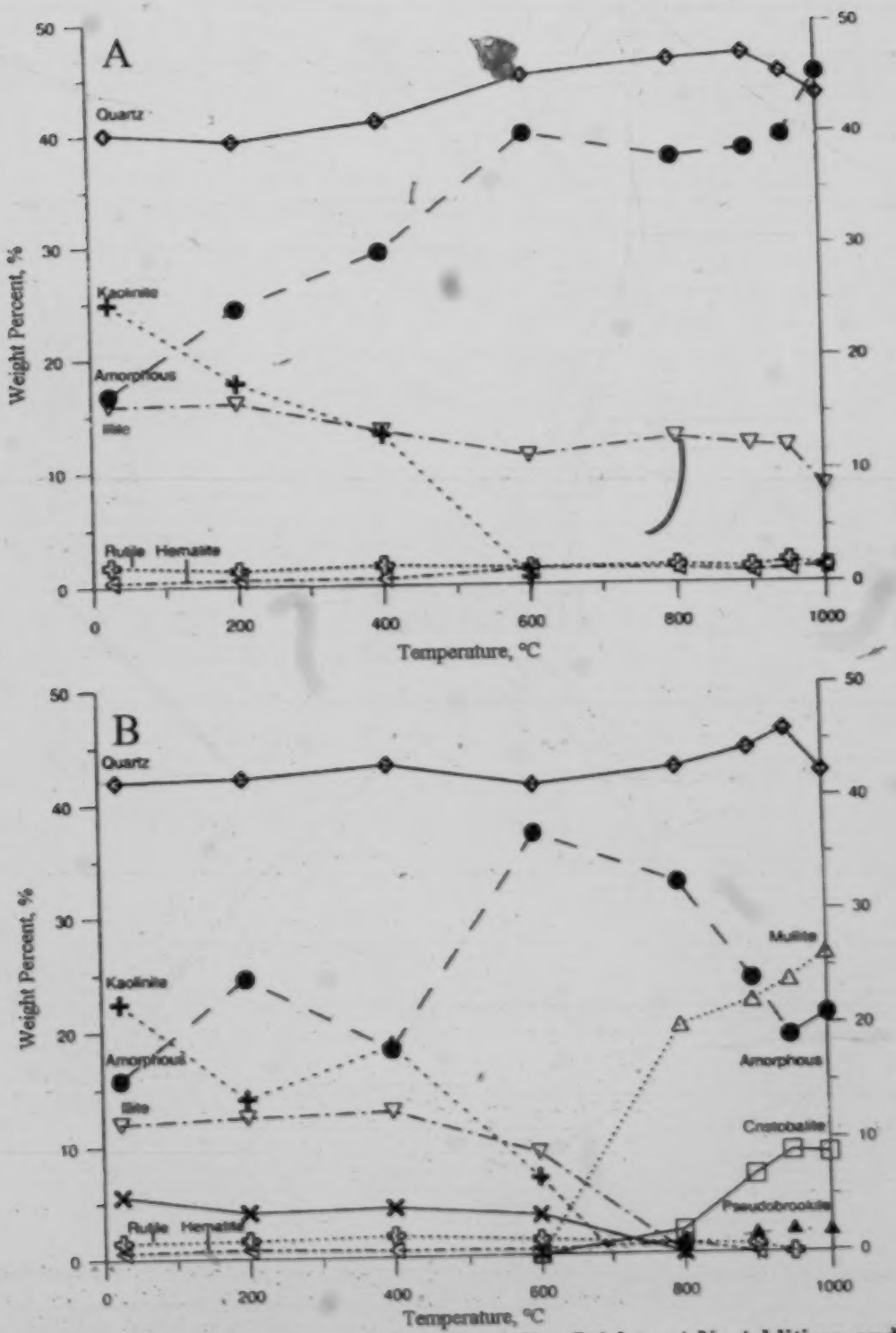


Figure 6.4 Phase Transformations in Fired Clay Bricks – a) No Additives, and b) Clay Doped with 5% V_2O_5 (234)

Stoichiometrically, there is more iron in the Suncor ash than could be contained in the pseudobrookite structure, given the amount of titanium present in the ash. Thus, it is likely that the remainder of the iron in the ash has been incorporated into the mullite-type phase ($Na_2Al_{2x}O_{3x+1}$), as mullite formed under similar conditions is reported to contain significant concentrations of iron (234).

Schneider (39) indicated that the Suncor ash required temperatures greater than 1450°C to melt, which would be consistent with the presence of mullite in the ash. However, contrary to previous inferences, the high melting temperature is likely the result of the transformation of the ash to mullite, cristobalite and pseudobrookite during heating of the ash samples for those tests. Thus, the original melting temperature of the ash minerals to form cenospheres is believed to be much less than 1450°C.

6.2.1.1 Comparison with Previous Testwork

Griffin reported that roasting Suncor fly ash at 800°C increased the vanadium extraction from the ash to as high as 6%, 54%, 30%, and 38% when leaching with water, H_2SO_4, NaOH, and Na_2CO_3, respectively (185). This compares with water leach extractions of between 20 and 40% vanadium from this testwork. It is possible that the presence of carbon during heating at 800°C may have affected the phases formed, or the oxidation of the vanadium in those minerals, which resulted in less water soluble vanadium in Griffin's ash samples.

6.2.2 Roasting with NaCl

The relationship between vanadium extraction and the three major roasting parameters (salt addition, roasting time and temperature) on the salt roasting of various Suncor fly ash samples is summarized in Figures 6.5, 6.6 and 6.7.

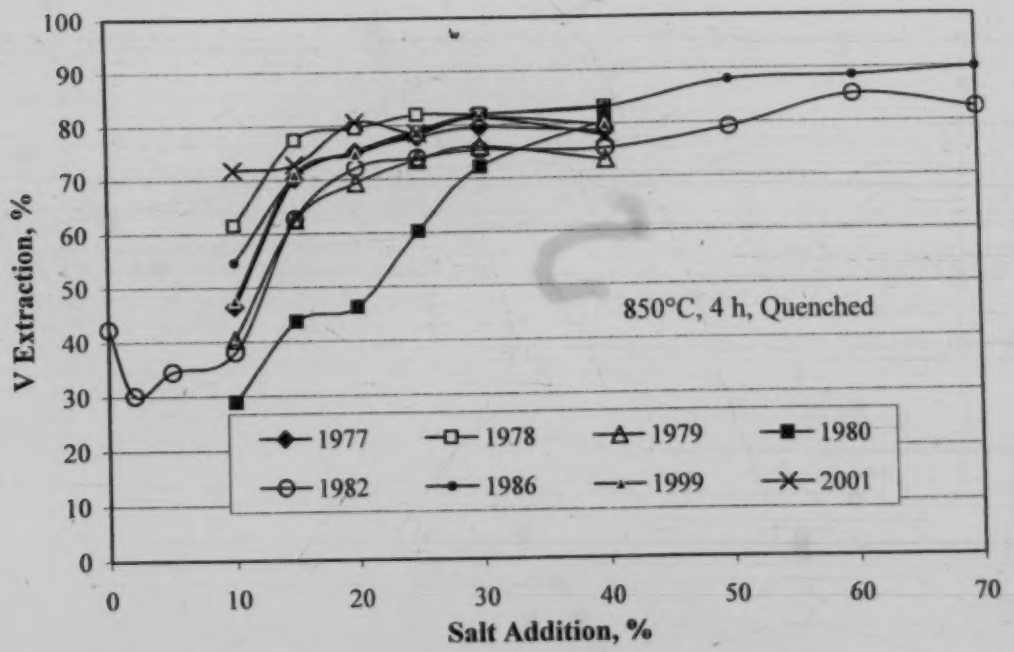


Figure 6.5 Effect of Salt Addition on the Roasting of Suncor Ash

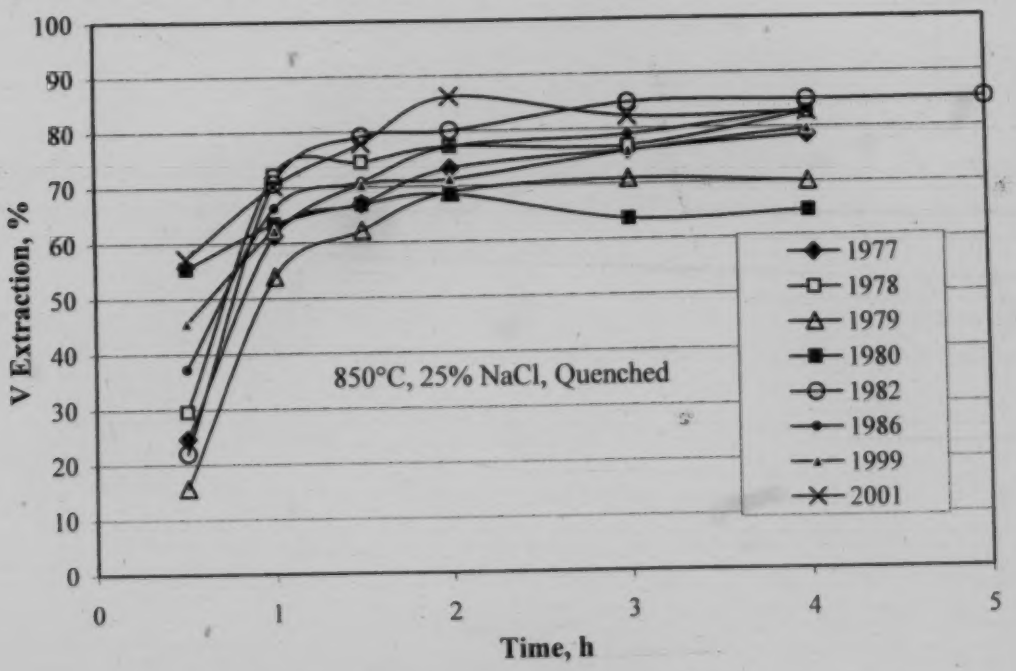


Figure 6.6 Effect of Time on the Roasting of Suncor Ash

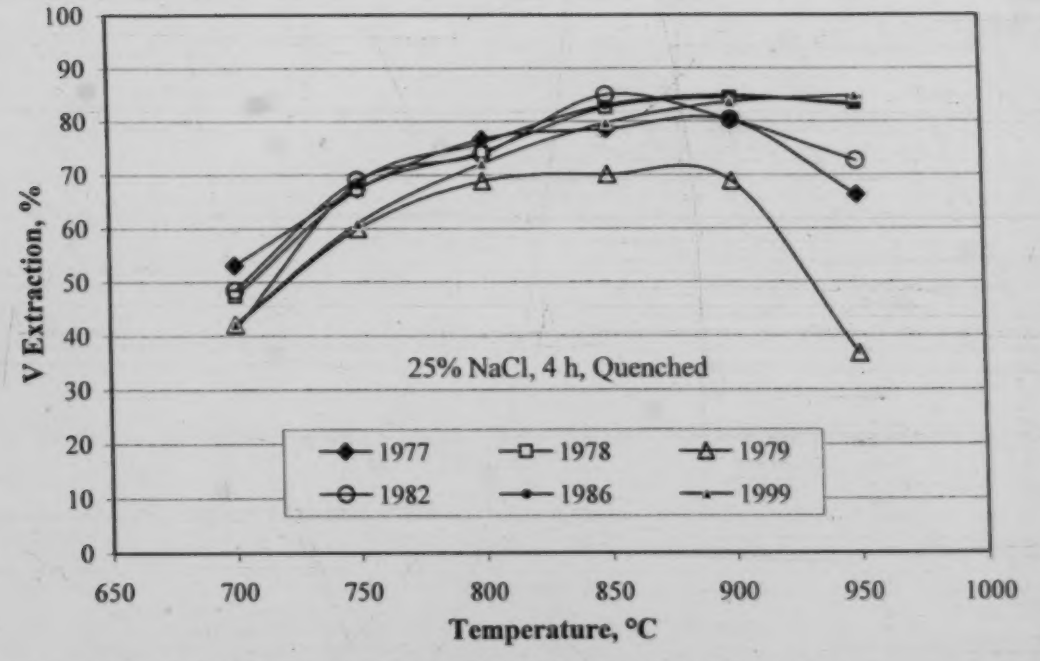


Figure 6.7 Effect of Temperature on the Roasting of Suncor Ash

The vanadium extractions for the ash samples from 1977 to 2001 plateau at between 75 and 85%. In the samples tested, the optimum roasting conditions were 20 to 30% NaCl, and 2 to 3 h roasting at 850 to 900°C. Considering the variability that would be expected from spot sampling 25 years of production, these tests indicate that the Suncor fly ash shows remarkable consistency in its response to salt roasting.

In some cases, tests were conducted using very high (50 to 70%) and very low salt additions (0 to 10%), which were outside the range of additions reported in earlier testwork. (39,185,187). Very high additions of salt result in vanadium extractions approaching 85 to 90%, while lower additions appear to show a transition between the roasting response observed when roasting without NaCl and roasting with NaCl at the optimum roasting conditions.

One fly ash sample that varies slightly from the above trends is the 1980 sample which is believed to be an example of upset conditions in Suncor's boilers as the ash contained very high levels of carbon and had a much lower bulk density than the other fly ash

samples. As shown in Section 3.1.2, the SEM micrographs of the 1980 ash sample do not show any significant departure from the structures observed in other ash samples. Similar vanadium extractions are achieved for this sample, but higher salt additions are required. It is possible that this sample was produced during a period of low temperature operation or higher flow rates, either of which could be the cause of the high carbon content in this ash, and the slightly different behaviour during salt roasting.

Several samples, specifically the 1977, 1979 and 1982 samples, do show a significant drop in the vanadium extraction as the roasting temperature was increased from 900 to 950°C. Some researchers have proposed, that the higher temperature would allow for faster melting and increased fluidity of the NaCl, which, as a low viscosity liquid phase, could interfere with oxygen transfer during the reactions in salt roasting (102,185). However, since the optimum vanadium extractions are achieved at temperatures greater than the melting point of NaCl (i.e., 801°C), and some samples show no drop in the vanadium extraction at 950°C, the cause for this behaviour in some ash samples is uncertain.

Two tests were also conducted to further look at the effect of operating temperature on the optimum salt addition and the results from these tests are shown in Figure 6.8. Roasting at 750°C required the addition of 15 to 20% more salt to achieve similar extractions to those achieved at 850°C. With the exception of the 20% NaCl sample, roasting at 900°C gave similar vanadium extractions to those achieved by roasting at 850°C for salt additions less than 30%, and higher extractions of up to 90% for salt additions of 40 to 50%. This indicates that similar vanadium extractions are possible above and below the melting point of NaCl, but that adjustments to salt addition may be necessary to maximize vanadium extractions for different operating temperatures.

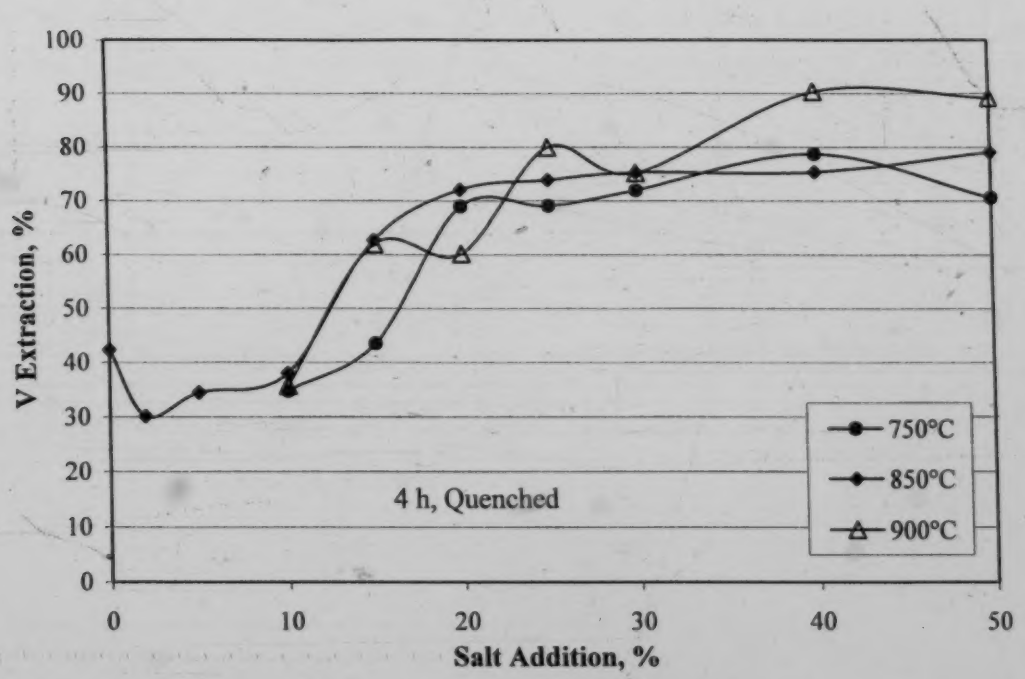


Figure 6.8 Effect of Temperature on Salt Addition in the Roasting of Suncor Ash

6.2.3 Side Reactions

Many vanadium studies have been concerned with controlling side reactions which limit, or lower, the vanadium extractions. These reactions are generally believed to be sensitive to extended roasting times or to the cooling rate of roasting samples (11). No difference was observed between the extractions from samples that were air cooled or quenched in this study, though furnace cooling has been reported to lower vanadium extractions (39). In addition, the Suncor ash does not appear very sensitive to roasting time, as the vanadium extractions do not vary significantly between 2 and 5 h of roasting (Figure 5.2).

The formation of vanadium bronzes has been cited largely for feeds, such as titanomagnetite ores and vanadium slags, in which vanadium is present, at least in part, as V^{3+} or V^{4+}. As the formation of vanadium bronzes requires vanadium to be present both as V^{4+} and V^{5+}, it is unlikely that vanadium bronzes could be formed, under even mildly oxidizing conditions, when roasting ores containing vanadium predominantly as V^{5+}. For the Suncor fly ash, preroast leaching tests indicate that at least 40 to 50% of the vanadium

is present as V^{5+}. This combined with the insensitivity of the Suncor fly ash to roasting times or cooling rate, likely indicate that, in the decarbonized ash, all of the vanadium available by salt roasting is present as V^{5+} or is oxidized to V^{5+} during roasting.

In studies on salt-roasting of carnotitic sandstones, high levels of quartz are cited to increase the salt consumption, and increase silica dissolution, through the formation of sodium silicate compounds (53,54). Even with the presence of almost 60% SiO_2 in some of the samples, the dissolution of silicon with water leaching remained very low in these tests. The formation of aluminosilicates during roasting is presumed to limit the amount of free quartz available to undergo this reaction.

6.2.4 Solution Composition

A typical leach solution from the salt roasting tests contains (mg/L): 12000 to 20000 V, 2 to 35 Al, 5 to 10 Fe, 300 to 600 Mo, 10 to 100 Ni, 40 to 110 Si and 0 to 10 Ti. Sodium and potassium were analyzed in one leach solution sample to contain around 10 g/L Na and 3.2 g/L K. Thus, the leach solution contains relatively low levels of contaminants, except for molybdenum, potassium and sodium. A detailed analysis of the solution composition is included in Section 9.0.

6.2.5 Effect of Carbon on Vanadium Extraction

Several researchers indicate that the presence of unburned carbon is detrimental to the recovery of vanadium by salt roasting, possibly due to the reduction of vanadium to V^{4+} or V^{3+} by carbon which could then form water-insoluble vanadium compounds (39,52,53,163,164,187-189,190,191,192). However, another researcher indicates that small additions (1 to 3%) of certain carbonaceous materials during salt roasting can improve vanadium extractions (172). Few, if any, attempts have been made to define the maximum allowable carbon for salt roasting a given material before the vanadium extraction is affected.

To better understand the effect of unburned carbon on the vanadium extraction, one test series was conducted to delineate the effect of carbon during salt roasting. As-received and "carbon-free" fly ash samples from 1986 were combined to give nominal carbon contents ranging from 0 to 25% and salt was added to the mixture to give a salt addition of 25%, based on the total weight of "carbon-free" fly ash in each sample. The results of this test are shown in Figure 6.9.

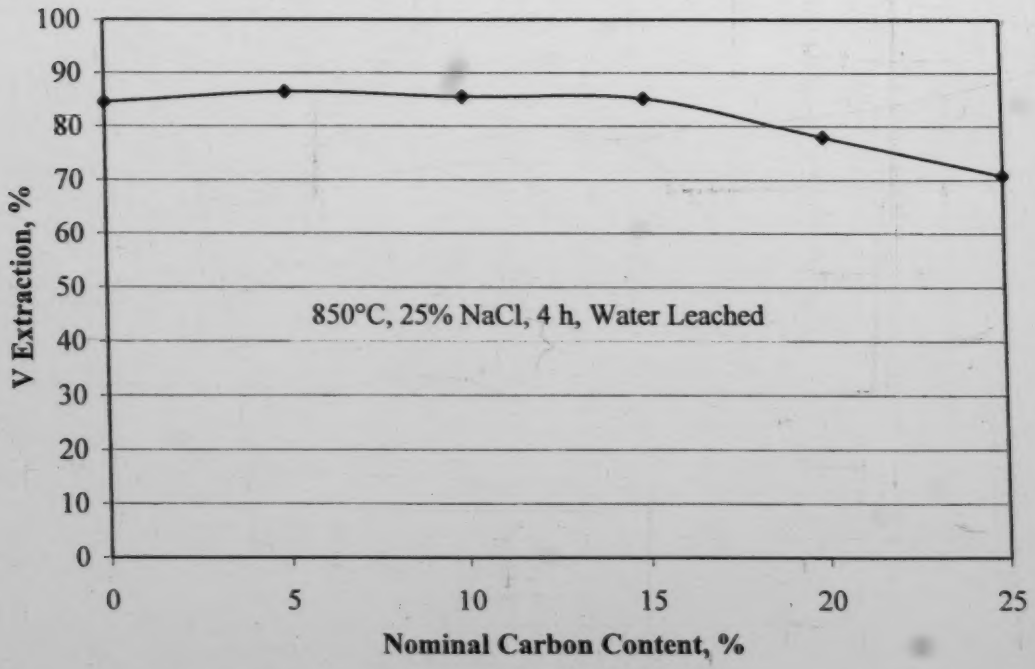


Figure 6.9 Effect of Carbon on Vanadium Extraction

Virtually no change in vanadium extraction was observed until the ash contained more than 15% unburnt carbon. This may indicate that carbon need not be completely removed during the decarbonizing roast.

In industrial application, this behaviour is encouraging for two reasons. First, minor fluctuations in the operation of the decarbonization furnace are unlikely to affect the extractions in salt roasting because low concentrations of carbon in the feed to salt-roasting can be tolerated. Second, it may be possible to burn a portion of the carbon in the fly ash during salt roasting, which could be used to improve the heat balance and

lower the fuel and heating requirements in that process step. (Partial oxidation of the carbon could also reduce the required size of the decarbonization furnace.)

6.3 Repulp Tests

A few additional tests were conducted to determine whether the vanadium extraction could be improved by leaching of the residue from salt roasting in other lixiviants.

Preliminary tests indicated that increases in the vanadium extraction of 4 to 8%, depending on the sample, were possible with either 100 g/L Na_2CO_3, 100 g/L NaOH, or 178 g/L H_2SO_4. Leaching with Na_2CO_3 was selective to vanadium while both NaOH and H_2SO_4 leached significant concentrations of Al and Si from the ash. Leaching with lower concentrations of H_2SO_4 (10 g/L) lowered the amount of Al and Si dissolved, but only increased the vanadium extraction by 2 to 3%.

Further testing indicated that the increase in vanadium extraction with other lixiviants varies slightly from sample to sample. For example, leaching with sodium carbonate increased the vanadium extraction by 2 to 5% for the 1986 sample and 3 to 10% for the 2001 sample to give maximum overall extractions of 85 to 86% (compared with water leach extractions of 81 to 83%). Generally, greater relative increases in the vanadium extraction were observed for samples roasted with lower salt additions. Leaching with sodium sulphate also gave minor improvements in the vanadium extraction for the 2001 sample, but this increase was generally 1 to 4% less than that achieved using sodium carbonate as the lixiviant.

Leaching in 100 g/L sulphuric acid increased the vanadium extraction by 5 to 15% for the 1986 sample and 11 to 17% for the 2001 sample, but the concentrations of Al and Si dissolved were between one and three times higher than the vanadium concentration in the leach solution, representing well over 100 times more Al and Si in the acid leach solutions than in the water leach solutions.

Based on these findings, leaching with sodium carbonate may be an option for maximizing the recovery of vanadium from the fly ash, while minimizing the concentrations of impurity elements in the leach solution.

6.4 Characterization

A combination of scanning electron microscopy (SEM) and x-ray diffraction analysis (XRD), along with the results from the leaching and roasting testwork, were used to gain an understanding of the chemical reactions involved in the salt roasting of the Suncor ash and of the structures present before and after salt roasting. Decarbonized fly ash was used for all the micrographs and in all the XRD analyses. The SEM micrographs are shown in Figures 6.10 to 6.14.

Scanning electron microscope micrographs of the fly ash before roasting (Figure 5.5) may provide an explanation for the consistency of the Suncor ash with time. The Suncor mineral portion of fly ash is made up almost entirely of aluminosilicate cenospheres; that is, all of the mineral components contained, or entrained, in the bitumen before coking have been combined into a single uniform phase. Contrary to previous reports no sign of microcrystals were observed (29,185). In some samples, distinct elongate anhydrite ($CaSO_4$) crystals are also observed in the as-received fly ash.

X-ray diffraction (XRD) patterns of this sample indicated that the structure of the cenospheres was poorly crystalline, with low intensity peaks corresponding to mullite ($3\ Al_2O_3 2\ SiO_2$). This could indicate that the cenospheres are largely composed of a metastable aluminosilicate glass, with small quantities of crystalline high-temperature aluminosilicates contained therein.

Compared with the ash from Syncrude (Section 8.0), the higher temperatures of the Suncor coking process appear to produce a more homogeneous fly ash with a higher degree of uniformity with respect to particle size and mineralogy than the Syncrude ash. This uniformity in structure, and the observed uniformity in roasting behaviour, indicates

that the Suncor ash would be a consistent vanadium feedstock for any proposed vanadium recovery plant.

After salt roasting the Suncor ash, most, but not all, of the cenospheres decompose into two major phases: a crystalline matrix of similar Al and Si content to the original ash, and very small crystals (up to 3 μm diameter and up to 10 μm long) which are enriched in iron and titanium. (Similar decomposition was noted in Section 6.2.1 for roasting the ash with no additives.)

As in the ash roasted without any additives, the iron-titanium phase was identified from the x-ray diffraction patterns of the roasted ash as pseudobrookite (Fe_2TiO_5), a mineral that is sometimes in nature found along with ilmenite and other Fe-Ti oxides in titanomagnetite deposits. The solid solution series of pseudobrookite-ferropseudobrookite (Fe_2TiO_5-$FeTi_2O_5$) is generally associated with advanced high temperature oxidation (240), which is consistent with the formation and stability of this mineral under the salt roasting conditions. Recent studies have also indicated that pseudobrookite forms preferentially at elevated temperatures over other iron-titanium compounds in the presence of vanadium (234).

Pseudobrookite is orthorhombic and, as such, forms elongate crystals which are consistent in appearance with the crystals observed with the scanning electron microscope. The cation sites in pseudobrookite are both octahedral, allowing for the substitution of Al, Mg, Mn and other cations of similar size in its crystal structure.(240) The relative quantity of these crystals in the sample appears to increase with increasing roasting temperature (Figure 6.14) and these crystals are present in the ash, both before and after water leaching to recover vanadium.

Hematite (Fe_2O_3) is also detected in the x-ray diffraction pattern. Because the fly ash sample analyzed by x-ray diffraction (Suncor 1982) contained an Fe:Ti mole ratio of over 2.9, it is likely that the iron in excess of the 2:1 Fe:Ti ratio required for the formation of pseudobrookite formed as hematite during crystallization from the glassy ash structure.

The aluminosilicate phase produced during salt roasting is considerably different than that of the ash roasted with no additives. The x-ray diffraction patterns indicate that the matrix is composed of a sodium-rich feldspar (albite ($NaAlSi_3O_8$)); Al and Si are present as AlO_4 and SiO_4 tetrahedra, with Na present in voids in the aluminosilicate structure to maintain a charge balance. The feldspar structure allows for a certain amount of flexibility as the structure can accept significant amounts of K and Ca, in addition to Na, in the interstices and a varying ratio of Al:Si. Thus, the actual composition of the observed structure is likely somewhere between that of albite and anorthite ($CaAl_2Si_2O_8$), which form a solid solution at high temperatures of the form $(Na,Ca)(Al,Si)_4O_8$. The need for sodium ions to react both with the vanadium to form sodium vanadates and with Al and Si to form the feldspar structure could explain the need for higher salt additions for roasting the oil sands fly ash than are generally reported for other materials, such as titanomagnetite ores or slags, that are low in Al and Si.

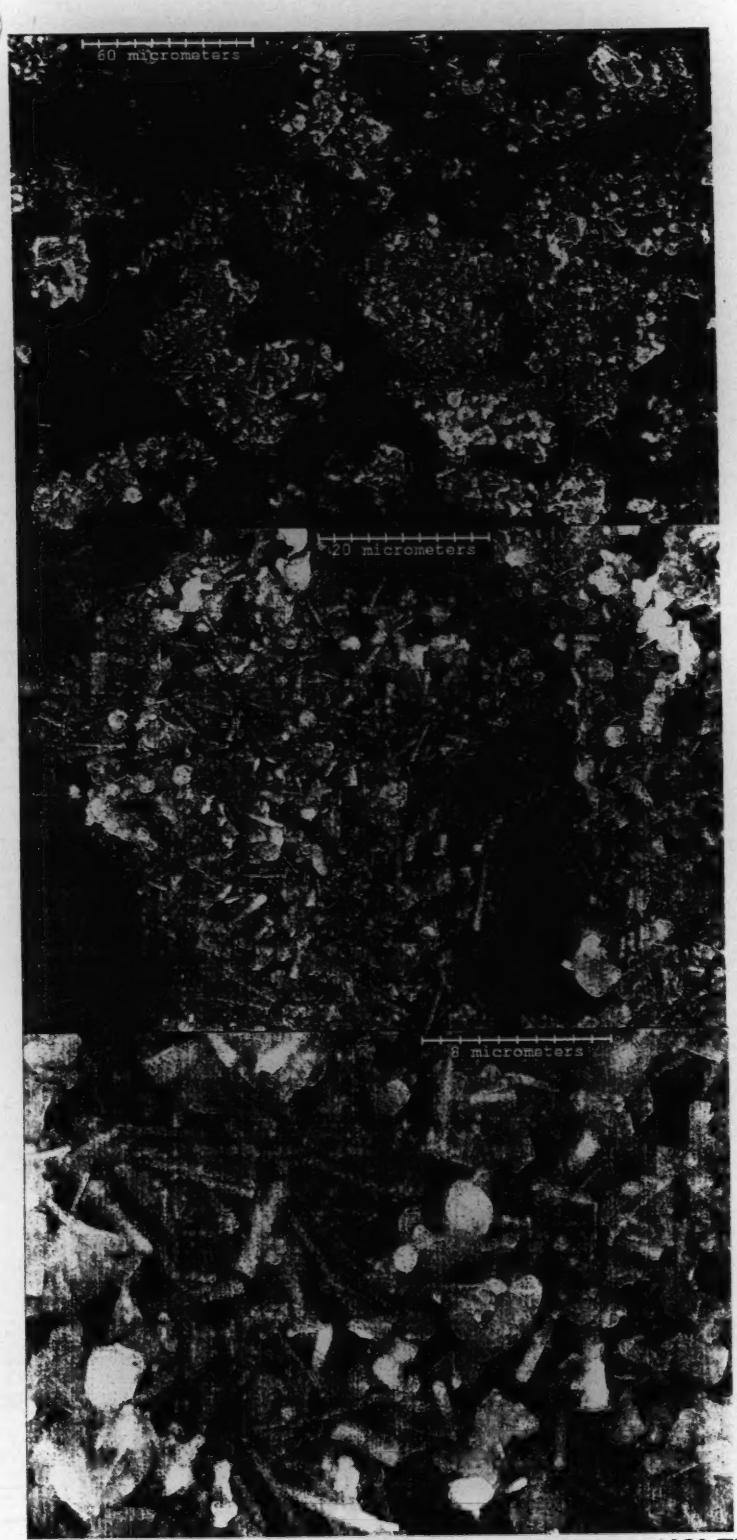
The remaining unidentified peaks in the x-ray pattern match the diffraction pattern for $Na_8Al_6Si_6O_{24}SO_4$, a feldspathoid mineral known as noselite. Feldspathoids generally form in the presence of a surplus of alkali metals and a deficiency of SiO_2. (241) Since in the Suncor fly ash, the Si:Al ratio ranges from 1.9 to 2.5, indicating a deficiency of Si for the albitic structure (Si:Al of 3:1), it is likely that a portion of the ash forms noselite to give an overall Si:Al ratio of around 2. The sulphate ions needed to form this phase likely come from anhydrite ($CaSO_4$) which was identified in some samples of the as-received ash, but was not detected in the x-ray patterns of the roasted ash.

Suncor 1979
500x Magnification

Suncor 1979
1500x Magnification

Suncor 1979
4000x Magnification

Figure 6.10 SEM Micrographs of Roasted Suncor 1979 Fly Ash Sample (Quenched)



Suncor 1980
500x Magnification

Suncor 1980
1500x Magnification

Suncor 1980
4000x Magnification

Figure 6.11 SEM Micrographs of Roasted Suncor 1980 Fly Ash Sample (Quenched)

Suncor 1982
500x Magnification

Suncor 1982
1500x Magnification

Suncor 1982
4000x Magnification

Figure 6.12 SEM Micrographs of Roasted Suncor 1982 Ash Sample (Air Cooled)

Suncor 1982
500x Magnification

Suncor 1982
1500x Magnification

Suncor 1982
4000x Magnification

Figure 6.13 SEM Micrographs of Roasted Suncor 1982 Ash Sample (Quenched)

Suncor 1986
500x Magnification

Suncor 1986
1500x Magnification

Suncor 1986
4000x Magnification

Figure 6.14 SEM Micrographs of Roasted Suncor 1986 Sample (950°C, Quenched)

Based on Figure 6.5, the shift from the formation of mullite to the formation of feldspar appears to require a minimum salt addition, with little change in the vanadium extraction for salt additions below 10%. Above that minimum salt addition, formation of albite, and the resultant improvement in vanadium extractions, is preferred and only small amounts of additional salt are necessary to produce a large increase in the vanadium extraction. The increase in vanadium extraction is likely a result of a lower solubility of vanadium in the feldspar structure, than in the mullite-type structure formed at low salt additions.

Thus, it appears likely that, on heating in the presence of sodium chloride, the fly ash decomposes with the majority of the Al, Si and other ions preferring tetrahedral coordination, along with the majority of the Na, K and Ca, reporting to the feldspar and feldspathoid phases and with the majority of the Fe and Ti and other ions preferring octahedral coordination reporting to the pseudobrookite or hematite phases.

Based on the x-ray diffraction patterns, it is uncertain which phase(s) the vanadium, molybdenum and nickel report to during this transformation as no XRD patterns for compounds containing V, Mo or Ni were identified from the XRD patterns of these samples. The ionic radii for V^{5+} and Mo^{6+} are very similar to the ionic radii for Al^{3+} and, thus, could form compounds in which V and Mo are in either tetrahedral or octahedral coordination, and, as such, could be present in the crystal structure of either the feldspar or pseudobrookite phases. Metamunirite ($NaVO_3$ or $Na_2V_2O_6$), a water soluble sodium vanadium compound that could be formed, is also orthorhombic with a similar crystal habit to pseudobrookite and, thus, could be present in the SEM micrographs without being able to distinguish the crystals visually from the pseudobrookite crystals. Very little information is readily available on the crystal structure of molybdates but, with the similarities of the deportment of vanadium and molybdenum during salt roasting and water leaching, it is likely that molybdenum and vanadium are largely present in the roasted ash as water soluble sodium vanadate or molybdate compounds.

To determine the association of V, Mo and Ni with the mineral phases in the roasted ash, a series of leaching tests using dilute leaching agents (10 g/L H_2SO_4 and 50 g/L NaOH) were performed on the water leach residue from the Suncor fly ash to try to selectively dissolve the aluminosilicate phases from the residue. The results of this testwork are shown in the following figure. (Dissolution is reported as a percentage of each element in the feed.)

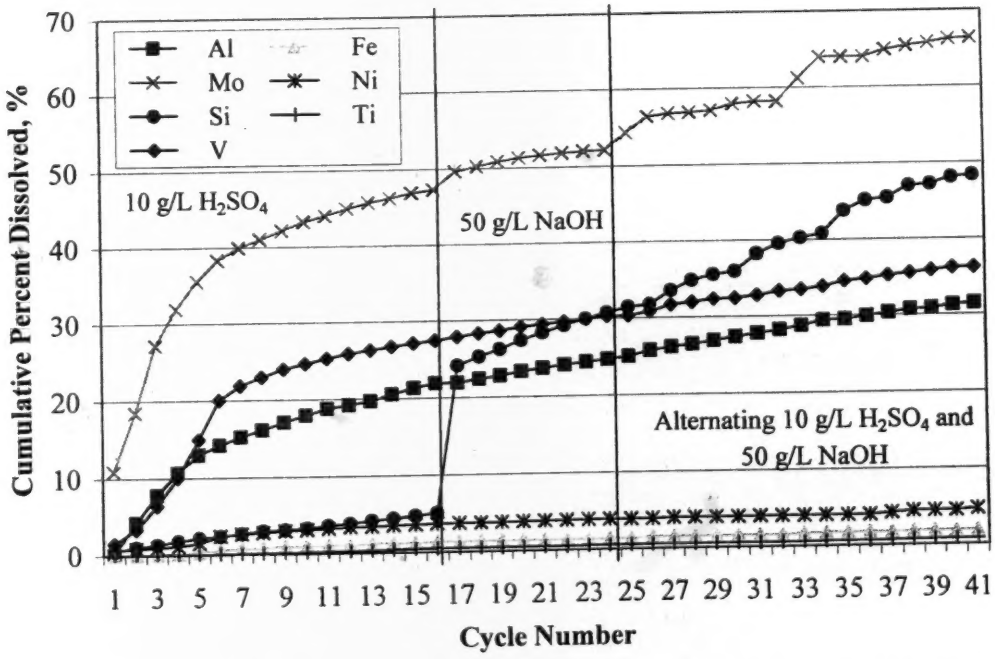


Figure 6.15 Cumulative Dissolution of Major Elements from Suncor Leach Residue

These tests clearly show that the dissolution of vanadium and molybdenum are associated with the dissolution of Al and/or Si, likely indicating that Mo and V in the leach residue are associated with the aluminosilicate phases in the residue. This behaviour agrees with the behaviour expected based on the size of the ionic radii of the V^{5+} and Mo^{6+} ions, which was discussed earlier. The limited substitution of vanadium into the feldspar matrix could possibly give a feldspar structure of the type $NaVAl_2SiO_8$, with vanadium substituting for Si, thus, requiring less interstitial calcium or sodium to maintain a charge balance due to the higher charge on the V^{5+} ion.

This may explain the possible relationship observed between the amount of calcium in the fly ash and the vanadium extraction, as the three ash samples with lowest Ca content also resulted in the three lowest overall vanadium extractions. It is possible that the low Si:Al ratio in the ash would favor the formation of anorthite ($CaAl_2Si_2O_8$) with a lower Si:Al ratio over an albite ($NaAlSi_3O_8$) and, thus, additional calcium would be more likely to lower the amount of vanadium retained in the feldspar structure. A higher calcium content in the ash could also correspond to higher sulphate content (i.e., $CaSO_4$) which could promote the formation of the noselite aluminosilicate phase. Preliminary tests on salt roasting a low calcium ash sample (Suncor 1982) with additions of 1 to 5% of $CaSO_4$, indicated that $CaSO_4$ additions of 1 to 2% increased the vanadium extraction by up to 2%, compared with samples which were salt roasted with no $CaSO_4$ added.

The association of vanadium with the aluminosilicate could also explain the slight improvements in the vanadium extractions observed with very high salt additions. It is possible that the addition of excess Na^+ ions could displace the V^{5+} ions from the feldspar matrix, and, thus, allow the formation of water soluble sodium- vanadium compounds. (This would require an excess of sodium, both to react with the feldspar mineral and the released vanadium, and, thus, the improvement in the vanadium extraction would be small for a large increase in the salt addition.)

The higher molybdenum extractions, compared with vanadium, during salt roasting may be a result of a lower solubility in the feldspar matrix, possibly due to higher charge of the Mo^{6+} ion.

Nickel, on the other hand, did not dissolve significantly and, therefore, would be presumed to be associated with the iron-titanium mineral (pseudobrookite) in the ash. Thus, if it was possible to selectively separate the pseudobrookite phase from the ash, an Fe, Ti and Ni concentrate might be produced from this material.

6.5 Magnetic Separation of Water Leach Residue

One scoping test was conducted to determine whether magnetic separation could be used to produce a magnetic concentrate enriched in Fe, Ti and Ni. In this test, water leach residue was ground to 90% passing 8 μm in a laboratory scale stirred ball mill and passed through a Davis Tube magnetic separator, which was borrowed from the Dynatec Corporation in Fort Saskatchewan, AB. A small amount of magnetic concentrate (0.15% of the residue weight) was obtained; the analyses for the magnetic and non magnetic fractions of the residue are shown in Table 6.2.

Table 6.2 Results of Magnetic Separation of Salt Roast Residue

Fraction	Al	Fe	Mo	Ni	Si	Ti	V
Magnetic	8.74	10.7	0.35	1.89	14.0	2.18	0.87
Non Magnetic	11.8	4.53	0.04	1.18	17.0	2.83	0.75

The borrowed Davis tube apparatus used a large permanent magnet and, thus, little could be done to optimize the configuration or intensity of the magnetic separator. Further research, such as optimizing grinding of the residue, measuring magnetic susceptibilities of the two phases and separation tests with a wet high intensity magnetic separator (WHIMS), would have to be performed to determine whether a higher grade Fe-Ti-Ni concentrate could be obtained.

6.6 Comparison with Previous Testwork

6.6.1 Griffin

Griffin's testwork indicated that fly ash, without prior decarbonization, could be combined with 14% salt and roasted at 900°C for 6 h to achieve an extraction of about 95% (185). Testwork to approximate the conditions reported by Griffin indicated that less than 20% vanadium extraction was possible with between 10 and 40% salt added. (This is lower than the vanadium extraction for samples from this research where the fly ash was roasted without any additives.)

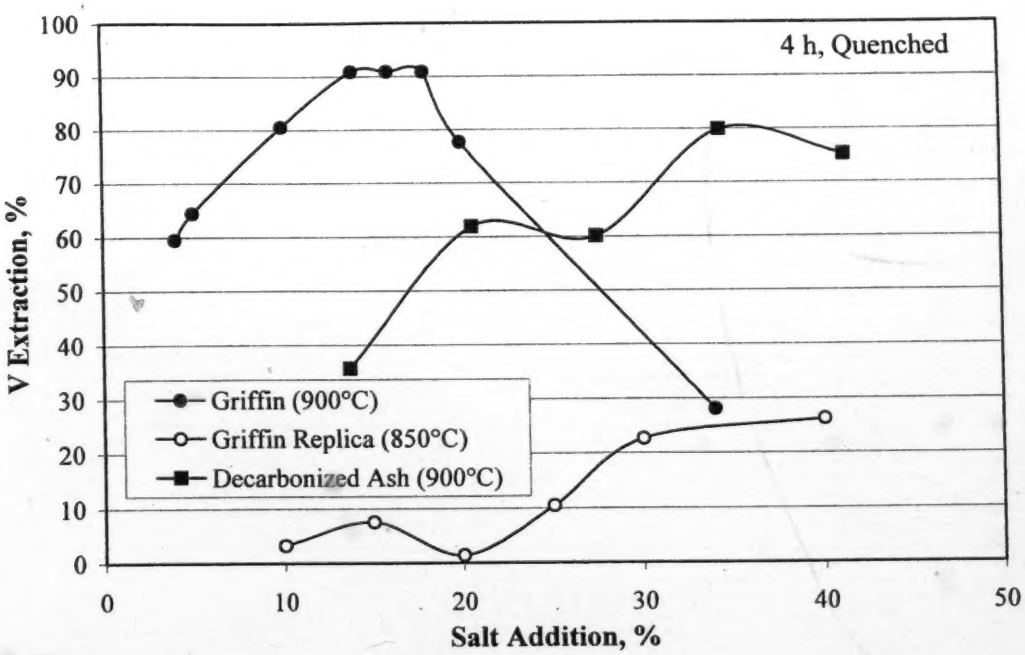


Figure 6.16 Comparison of Recent Tests with Griffin's Data

Similarly, tests simulating the conditions Griffin reported for reacting S° with as-received fly ash for the recovery of nickel resulted in less than 1% extraction of nickel and 60% V extraction, instead of 60 to 80% Ni and 30 to 50% V as reported by Griffin. As expected, the elemental sulphur added with the fly ash starting burning moments after placing the sample in the muffle furnace, with little noticeable SO_2 production after 10 minutes. Griffin also noted much more marked changes in vanadium extraction in response to changes in temperature and salt addition which were not reproduced in this testwork.

The data from these tests, combined with the observations made in Schneider's research, indicate that long heating times were used in all of the tests conducted by Griffin (39). That is, his roasting tests likely involved long enough times at low temperatures to burn most of the carbon before the reactions with salt began, and long enough times at low temperatures to allow S° to react with the ash before it could be burned to form SO_2. Even with a three hour heat-up time, or a nine hour total roasting time, Schneider (39) was unable to reproduce, or even approach, the extractions reported by Griffin, with maximum vanadium extractions of 60% reported by Schneider. It is also likely that the

more pronounced dependence of vanadium extraction on temperature and time reported by Griffin was also a result of the longer heating times required under Griffin's conditions and because increased temperature and longer times would also promote the decarbonization of the fly ash samples. Thus, at higher temperatures and longer times, carbon is more likely to be absent from the ash when the salt reacts with the ash and, thus, higher extractions would likely have resulted. The higher sensitivity of his results to the major roasting parameters (salt addition, temperature and time) can likely be also attributed to the presence of unburned carbon in the fly ash during salt roasting. The effect of carbon in the fly ash on the vanadium extraction is discussed in more detail in Section 6.2.5.

The increased sensitivity of vanadium extraction to changes in roasting conditions, compared with salt roasting of decarbonized ash, as well as the large increase in roaster capacity required to accommodate the longer roasting and gradual heating times, would make the application of Griffin's process to commercial operation unlikely.

6.6.2 Schneider

Compared with the rate curve proposed by Schneider (39), this study shows that the reaction rate for the vanadium extraction is faster than that reported by Schneider, and that lower overall vanadium extractions were achieved than indicated by Schneider (Figure 6.17). When roasting with salt and leaching with water, extractions of greater than 85% were seldom seen, except at very high salt additions, in this research. As well, Schneider indicated that higher salt additions lowered the vanadium extraction. This decrease, as shown in Figure 6.17, is slight and is likely due to analytical error; current tests indicate that increased salt addition results in either similar or higher vanadium extractions from Suncor fly ash.

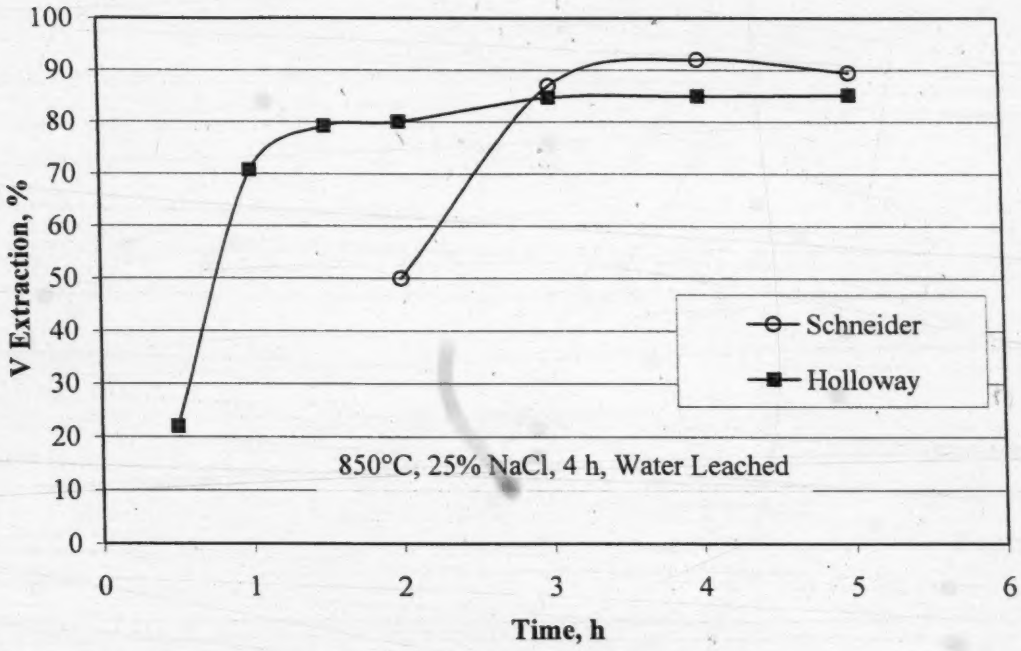


Figure 6.17 Comparison of Recent Tests with Schneider's Testwork

Overall, though, good agreement was reached between the present research and the research conducted by Schneider. This study involved more extensive testing of a wider range of fly ash samples, but confirms the optimum roasting conditions proposed by Schneider of 25 to 30% salt addition and 850°C.

As well, Schneider indicated that roasting the fly ash in moist air resulted in an extremely hard solid, suggesting partial melting or fusing of the ash sample during roasting. The presence of moisture in the air, and the presence of feldspar minerals in the ash could have resulted in the crossing of the "wet solidus" at the roasting temperatures which would lead to melting of the feldspar phase of the ash, or possibly in the formation of lower melting point hydrous aluminosilicates. (The presence of water along with feldspars and quartz can often lower melting temperatures below the melting temperatures usually observed in the absence of moisture.)

6.6.3 Gomez-Bueno et al.

There are several inconsistencies between the findings of Gomez-Bueno et al. (187,188) and the results obtained in this testwork. Their research did note the detrimental effect of high levels of carbon in the ash on vanadium extraction, but reported that essentially no water-soluble vanadium was formed during salt roasting. That result conflicts with the rest of the body of research on this material which indicates that water-soluble vanadium is readily formed under a wide range of salt roasting conditions.

In addition, extractions of over 80% were routinely reported with salt additions of 5 to 10% using a NaOH leach; with 10% salt, water extractions of only 40 to 70% were achieved from all of the Suncor samples tested in this research, with only minor improvements (2 to 4%) in vanadium extraction with sodium hydroxide leaching. The dissolution of silicon in the NaOH leach reported is very high, and consistent with the findings of this testwork, but would likely prohibit the use of this lixiviant commercially without the addition of ion exchange or solvent extraction circuits to the proposed flowsheet.

6.7 Conclusions

Salt roasting tests were conducted for Suncor ash samples collected over a 25 year period to determine the effects of time, temperature and roasting additions on vanadium recovery. The optimum roasting conditions were determined to be 2 to 3 h roasting at 850 to 900°C with NaCl additions of 20 to 30%, resulting in vanadium extractions of between 75 and 85%. These tests indicated that the response of the various Suncor ash samples to salt roasting is extremely consistent, making Suncor ash an excellent possibility as a feed for vanadium recovery.

Other factors that may influence vanadium recovery by salt roasting were also investigated. The effect of carbon in the ash on vanadium recovery was tested and ash with up to 15% carbon was shown to have no effect on vanadium extractions. After testing several different lixiviants, leaching with Na_2CO_3 was identified as an alternative

to water leaching as it improved vanadium extractions by 2 to 4% at the optimum roasting conditions, while selectively leaching vanadium.

Leach solutions from salt roasting tests typically contained (mg/L): 14000 to 22000 V, 3 to 35 Al, 5 to 15 Fe, 300 to 600 Mo, 10 to 140 Ni, 3200 K, 10000 Na, 40 to 100 Si and 0 to 20 Ti. Thus, the solution from salt roasting contains relatively low levels of most contaminants, except molybdenum and sodium, which should allow for the production of high grade vanadium products with little additional solution purification.

Characterization work, using a combination of x-ray diffraction, scanning electron microscopy, and diagnostic leaching tests, was also performed and, for the first time, a good understanding of the mechanism behind salt roasting of the oil sands fly ash to recover vanadium was attained. It appears that most of the components in the Suncor fly ash are initially present as cenospheres, which are believed to be made up of an amorphous aluminosilicate glass. These spheres, on heating, will crystallize with elements preferring tetrahedral coordination reporting to aluminum- or silicon-rich phases and with elements preferring octahedral coordination reporting to iron- and titanium-rich phases. Without any additives, the cenospheres break down during roasting to form $Na_2Al_{2x}O_{3x+1}$, a mullite-type structure, cristobalite, a high temperature polymorph of SiO_2, and pseudobrookite (Fe_2TiO_5). (Vanadium, and some of the silicon and iron, are believed to substitute for aluminum in the mullite-type structure.) Roasting with NaCl results in the formation of slightly different minerals with Al and Si reporting to either an albitic feldspar ($NaAlSi_3O_8$) or noselite ($Na_8Al_6Si_6O_{24}SO_4$) and Fe and Ti crystallizing as either pseudobrookite or hematite (Fe_2O_3). The portion of the vanadium and molybdenum which is not rendered water soluble during salt roasting is believed to be associated with the aluminosilicate minerals, while the majority of the unleached nickel is believed to report to the pseudobrookite phase. (Magnetic separation of finely ground salt roast residue produced a small amount of material enriched in Fe, Ti and Ni.) The large difference in extraction, roasting with and without salt, is believed to be related to differences in vanadium solubility in the aluminosilicate minerals formed during roasting and the availability of sodium for the formation of water-soluble vanadium compounds.

7.0 Roasting Suncor Ash with Alternative Reagents

The optimum salt addition for the Suncor ash is high, relative to the salt additions reported for various other vanadium-bearing materials, and the overall extraction at 75 to 85%, though typical, is lower than the greater than 90% that would be desirable in commercial operation. Thus, to investigate alternatives to roasting with NaCl, tests were conducted where Suncor fly ash was roasted with the addition of various alternative roasting reagents, such as Na_2CO_3, Na_2SO_4, $NaNO_3$ and CaO. (All these other reagents have been proposed for salt roasting of vanadium ores in the literature (Section 2.3.))

7.1 Roasting Tests

7.1.1 Roasting Additives

The vanadium extraction with increasing reagent addition for roasting 1982 Suncor fly ash at 850°C for 4 h are shown for these reagents in Figure 7.1.

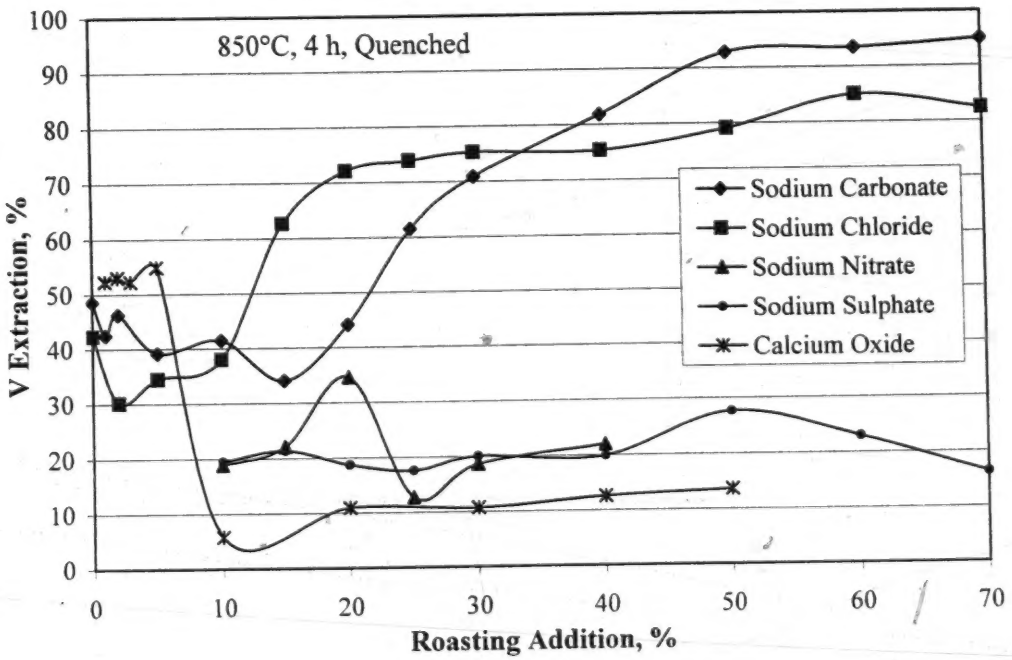


Figure 7.1 Effect of Various Roasting Additives on Vanadium Recovery

Up to 95% extraction of vanadium was possible with very high additions of sodium carbonate (i.e., 50 to 70%). The leach solution from sodium carbonate roasting contained comparable levels of most impurities to the leach solution from salt roasting, but with about three times more aluminum in solution (i.e., up to 25 mg/L). This indicates that Na_2CO_3 could be used as an alternative reagent to NaCl, and could give slightly higher vanadium extractions, but would require higher reagent additions than roasting with NaCl.

With the exception of Na_2CO_3, the alternative reagents tested produced lower vanadium extractions than were achieved with NaCl, and, in most cases, lower extractions than roasting without any reagents (Figure 6.1).

Roasting with a mixture of $NaNO_3$ and NaCl, combined to give a total of 25% additive by weight, also proved ineffective. No change in the vanadium extraction was evident for 0 to 5% $NaNO_3$ (20 to 25% NaCl), but, above 5% $NaNO_3$, the vanadium extraction decreased gradually from the maximum of 80% at 25% NaCl to a minimum of 11% at 25% $NaNO_3$. In this test, the behaviour exhibited during roasting with either NaCl or $NaNO_3$ individually was not apparent. Instead, the end result appears to be more of a "hybrid" of the two effects, possibly indicating that the sodium nitrate and sodium chloride react with the ash with two different, and possibly competing, reaction mechanisms.

7.1.2 Roasting Temperature

Roasting at 950°C with Na_2CO_3 and Na_2SO_4 further depressed the vanadium extraction (Figure 7.2). The highest extractions at 950°C with Na_2CO_3 and Na_2SO_4 were 45% and 20%, respectively. In addition, at 950°C, high additions of Na_2CO_3 resulted in melting of the roasted ash and increased dissolution of Al and Si during water leaching. Very little, except very low levels of V, Mo and Si, was leached from the fly ash roasted with sodium sulphate at 950°C.

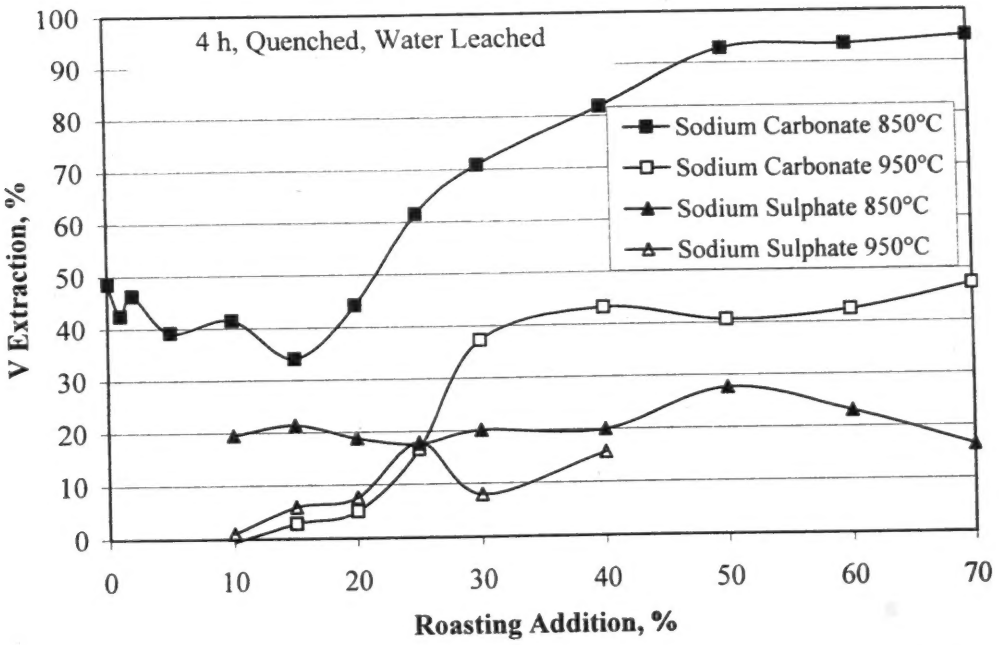


Figure 7.2 Effect of Temperature on Sodium Carbonate and Sulphate Addition

When roasting at 850°C with Na_2CO_3, the sodium carbonate is very close to its melting point, which is 851°C for pure Na_2CO_3. Unlike the reaction with NaCl, which appears to be improved above the melting temperature of NaCl, increasing the roasting temperature for sodium carbonate significantly above its melting temperature appears to have a detrimental effect on the extraction. At 950°C, the increase in vanadium and silicon extraction observed at higher Na_2CO_3 additions could indicate that a sodium silicate ($NaSiO_3$) glass is formed under these conditions. (Sodium silicate would have a much higher solubility in water than the silicate structures formed at 850°C.) Sodium carbonate is a well-known flux for reducing the melting point of silicates (242); in these tests, high additions of Na_2CO_3 at 950°C resulted in melting of the ash samples. The formation of a more glassy, lower melting point aluminosilicate phase, though slightly better than the mullite type phase achieved by roasting without any additives in terms of vanadium extraction, did not provide an adequate separation of vanadium, in a water soluble form, from the other components in the ash.

The addition of Na_2SO_4 caused severe sintering of the fly ash, especially at higher additions. Ash samples often show a reduction in apparent volume, likely as a result of a decrease in void space due to changes in mineralogy and sintering during roasting. However, the ash samples generally "sink" and still maintain the shape of the crucible. However, with the addition of sodium sulphate, the ash "coalesces" to form a pellet where only the very bottom of the sample remains in contact with the walls of the crucible. The sintered Na_2SO_4 samples were extremely difficult to fracture, requiring the use of a hammer to reduce the particle size to allow leaching of the roasting samples of ash to take place.

The decrease in the extractions for roasting with Na_2SO_4 at 950°C may also be a result of melting of the sodium additive as the melting point for Na_2SO_4 is 885°C. Though apparently the addition of sodium sulphate had little effect on the vanadium extraction, relative to the samples roasted without any additives, the melting of the sodium sulphate furthered reduced those low extractions, possibly by preventing the formation of water soluble vanadium during decomposition of the ash, or by occluding the water soluble vanadium compounds with the melt so that they were unavailable to water leaching. Hence, it may be possible to realize similar extractions to those achieved by roasting with Na_2SO_4 at 850°C, if the particle size of the roasted ash could have been reduced further prior to leaching.

7.1.3 Solution Composition

Roasting with sodium carbonate or sodium sulphate, followed by water leaching gave a similar solution composition to roasting with NaCl for most of the major impurities, except that high soda and sodium sulphate additions led to increases in the extraction of aluminum (Na_2CO_3) and nickel (Na_2SO_4). The solubility of all major impurities in water decreased markedly with increasing additions of $NaNO_3$.

Roasting at 950°C with high soda additions further increased the solubility of Al and Si in water while the solubility of most elements decreased when roasting with Na_2SO_4 at 950°C, resulting in only low levels of V, Mo and Si in solution.

From 0 to 5% addition of CaO, the leach solution contains similar levels of impurities as observed in the water leach solution from samples roasted with NaCl but, above 5%, essentially none of the major elements, except for very small amounts of V and Mo are leached with water. This behaviour is reasonable since CaO is used as an additive (~9 wt%) to soda-silica glasses to reduce the water solubility of sodium-silicon glasses (242).

7.2 Repulp Tests

Other leaching reagents (100 g/L Na_2CO_3 and 100 g/L H_2SO_4) were tested to determine whether the vanadium extraction from these tests could be improved. The vanadium extractions from these repulp tests, as well as the extractions from water leaching, are shown in Figures 7.3 to 7.6.

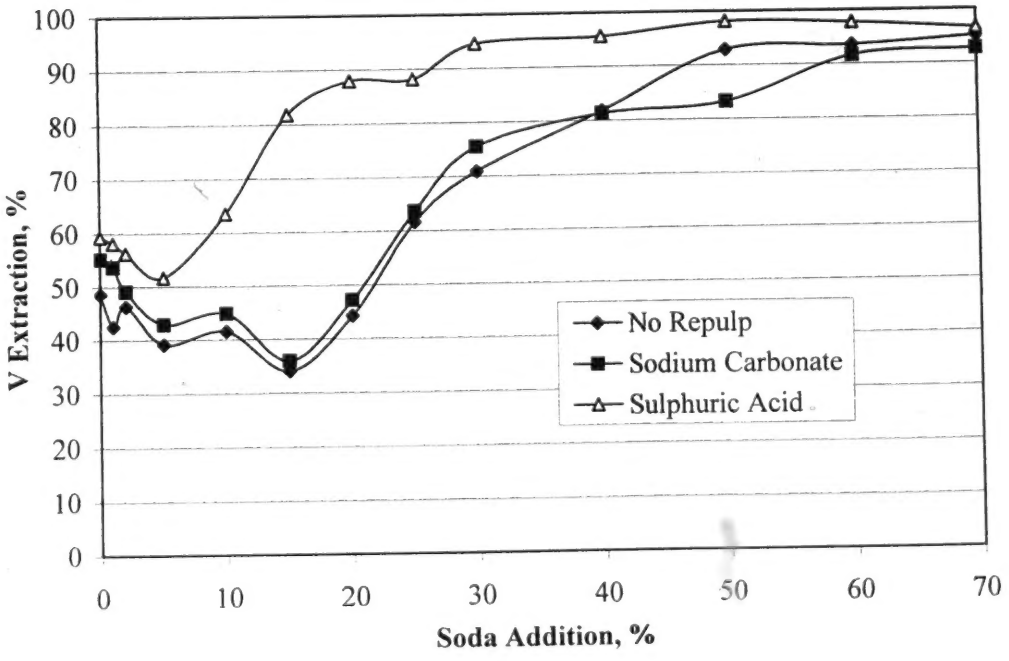


Figure 7.3 Effect of Leaching Reagents on Vanadium Extraction from Fly Ash Roasted with Sodium Carbonate

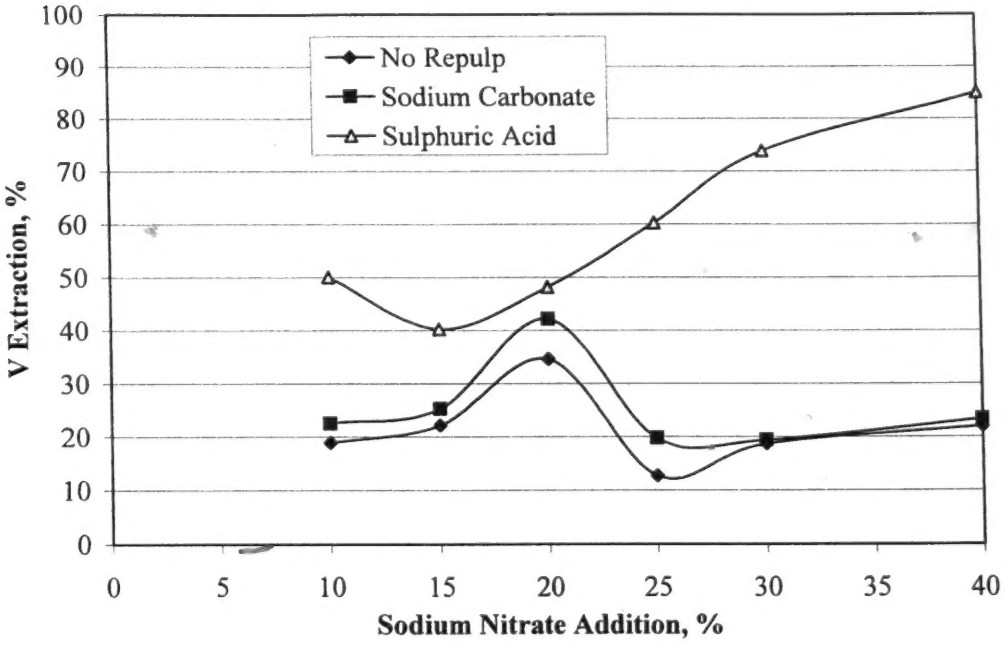


Figure 7.4 Effect of Leaching Reagents on Vanadium Extraction from Fly Ash Roasted with Sodium Nitrate

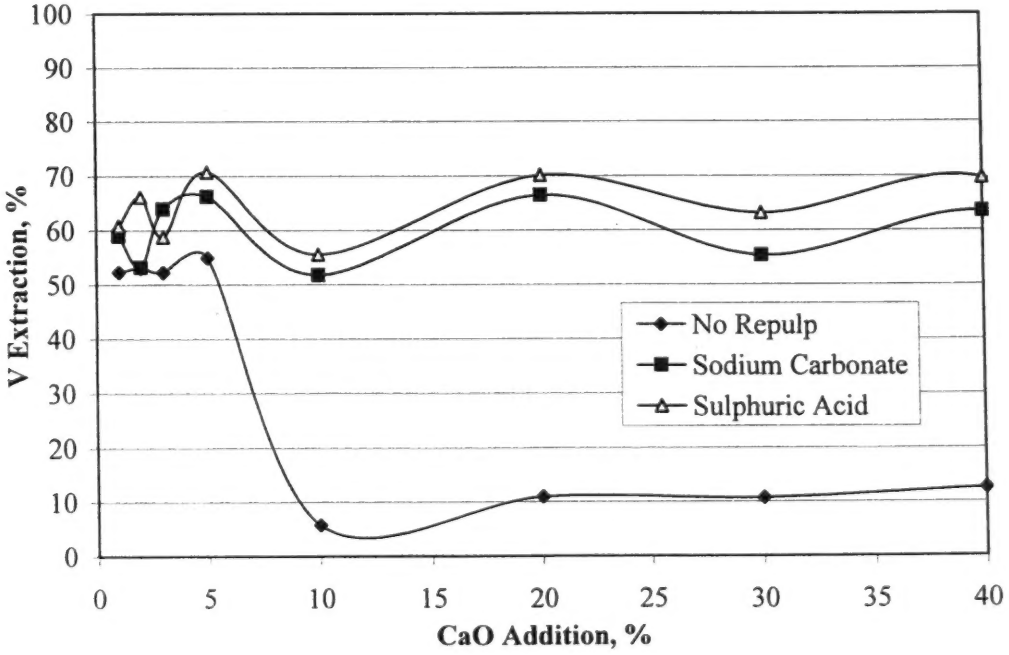


Figure 7.5 Effect of Leaching Reagents on Vanadium Extraction from Fly Ash Roasted with Calcium Oxide

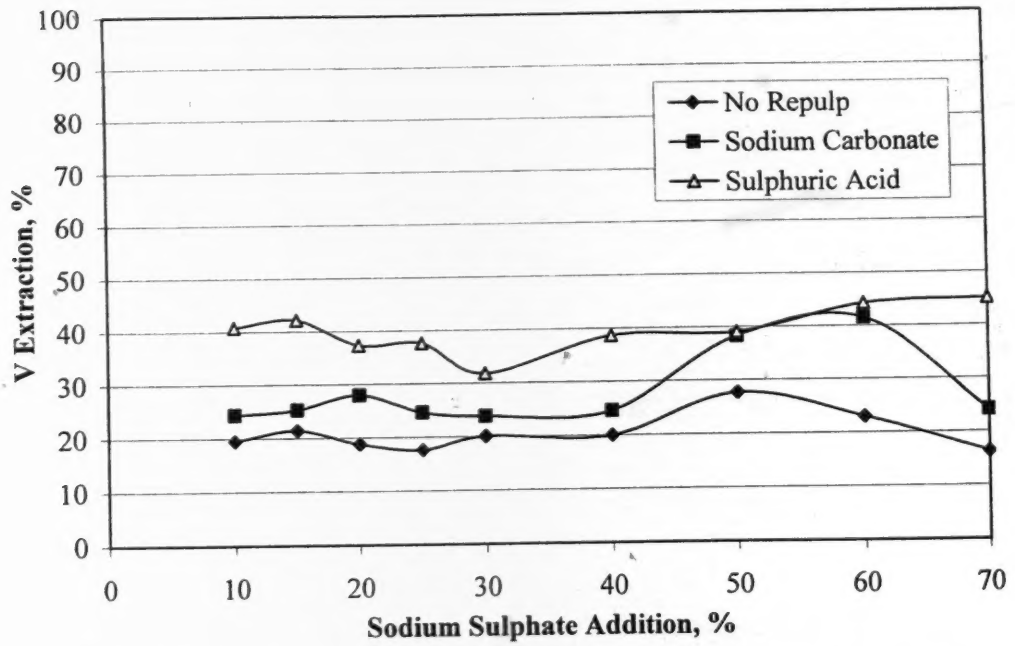


Figure 7.6 Effect of Leaching Reagents on Vanadium Extraction from Fly Ash Roasted with Sodium Sulphate

Leaching the roasting residues in 100 g/L Na_2CO_3 gave small improvements in extraction for the samples roasted with Na_2CO_3 (0 to 5%) and $NaNO_3$ (1 to 7%). These improvements are similar in magnitude to the improvements observed for the Suncor ash roasted with NaCl (2 to 10%). The increase in extraction was slightly higher for samples roasted with Na_2SO_4 as samples roasted with 10 to 40% Na_2SO_4 showed an increase from 4 to 9%, and the samples roasted with 50 and 60% Na_2SO_4 gave similar extractions to acid leaching (i.e., an 8 to 19% increase). For the samples roasted with CaO, leaching with Na_2CO_3 resulted in similar extractions to acid leaching (i.e., 50 to 70% for all CaO additions), and the solution contained only slightly higher levels of impurities than from water leaching.

Leaching the residue from these tests in 100 g/L H_2SO_4 increased the vanadium extraction to as high as 98% for Na_2CO_3, 50% for Na_2SO_4, 70% for CaO, and 85% for $NaNO_3$, but, in all cases, significant amounts of Al and Si and, in some cases, Fe were also leached into solution. Between 50 to 70% of the weight of the samples roasted with

sodium carbonate dissolved during acid leaching while some samples roasted with CaO showed a weight gain, despite the dissolution of significant amounts of Al and Si, likely due to the formation of $CaSO_4$ during leaching. (Fine white solids formed during leaching were visible in the acid leach residue for these samples.) In the samples roasted with $NaNO_3$, the degree of Al and Si dissolution was directly related to the solubility of vanadium, with the highest extractions seen in the samples with the highest extractions of Al and Si in the leach solution. (Much less Al and Si were dissolved from the samples roasted with Na_2SO_4, but much less vanadium was also extracted, possibly indicating that roasting with Na_2SO_4 causes the vanadium to report to an insoluble refractory phase.)

In all cases, improved vanadium extraction with acid leaching appears to be a result of chemical attack on another phase, presumably an aluminosilicate phase formed during roasting. Difficulties with solution purification and disposal, and the costs associated therewith, would likely discourage the use of acid leaching commercially.

7.3 Characterization

7.3.1 Sodium Carbonate

SEM micrographs of fly ash roasted with sodium carbonate were taken and are shown in Figures 7.7 and 7.8. Fly ash roasted with sodium carbonate forms similar structures to those visible after roasting with NaCl. Some cenospheres are still present, though most have a more dimpled appearance than those remaining after roasting with NaCl. Some elongate crystals are present, but they are much smaller and less prevalent than in the ash roasted with NaCl. In addition, both the dimpled cenospheres and the rest of the matrix contain more sodium than similar structures observed in the ash roasted with NaCl.

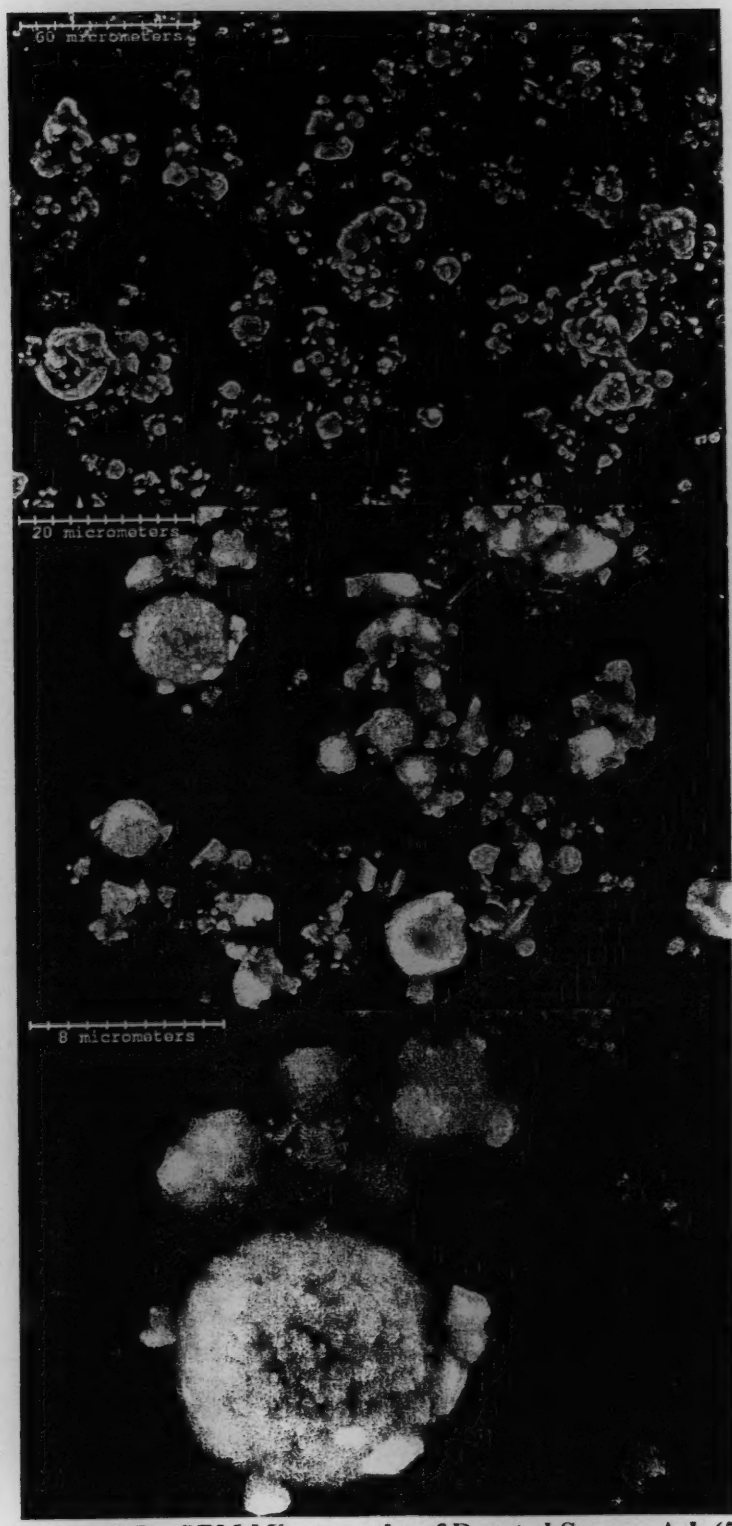
From the analysis of the ash after roasting with sodium carbonate with x-ray diffraction, the major aluminosilicate phases were identified as feldspathoids, predominantly nepheline ($(Na,K)AlSiO_4$), but with identifiable amounts of various cubic feldspathoid minerals, such as noselite ($Na_8Al_6Si_6O_{24}SO_4$), hauynite ($Na_4Ca_2Al_6Si_6O_{24}SO_4$) and lazurite ($(Na,Ca)_{4\text{-}8}(AlSiO_4)_6(SO_4,Cl)$), whose chemical compositions and XRD patterns

differ only slightly. (Sodalite ($Na_4Al_3Si_3O_{12}Cl$), the chloride form of the cubic feldspathoids, was not detected using XRD.) Cubic feldspathoids are commonly found in conjunction with nepheline deposits in nature (241). No minerals containing carbonates were detected.

Feldspathoids generally form under conditions with a surplus of alkali metals and a deficiency of SiO_2. Thus, these compounds generally contain higher levels of sodium than a similar feldspar mineral. (These feldspathoids have (Al+Si):Na ratios of 1.5 to 2, compared to an (Al+Si):Na ratio of 4:1 for albite.) Thus, the formation of feldspathoids may explain the need for higher doses of Na_2CO_3 to achieve high vanadium extractions, as a higher fraction of the sodium addition would be required to react with the aluminosilicate matrix.

The weight gain seen in the samples roasted with Na_2CO_3 support this theory. In the salt roasting tests, the final weight gain of the residue, after roasting and water leaching, was always within 5%, and generally less than 2%, of the original ash weight, likely as a result of volatilization of HCl that was formed during the roasting reactions and solubilization and dissolution of vanadium, molybdenum, and any unreacted salt from the ash during leaching. Roasting with Na_2CO_3, on the other hand, resulted in a significant gain in residue weight, with a range of weight gains from 5%, with 15% Na_2CO_3, added and up to 20%, with 70% Na_2CO_3 added. This weight gain is similar in magnitude to what would be expected if twice as much sodium were incorporated into the matrix of the ash.

The deportment of Fe, Ni and Ti in roasting with Na_2CO_3 is less clear than in the samples roasted with NaCl. The peaks for nickel titanate ($NiTiO_3$,, hexagonal) and bunsenite (NiO, cubic) can be identified with x-ray diffraction and hematite (Fe_2O_3) is also a possible phase, as the x-ray patterns of $NiTiO_3$ and Fe_2O_3 are very similar. Very few elongate crystals are observed in the SEM micrographs, indicating that pseudobrookite, or other orthorhombic or tetragonal minerals, are largely absent from this sample.

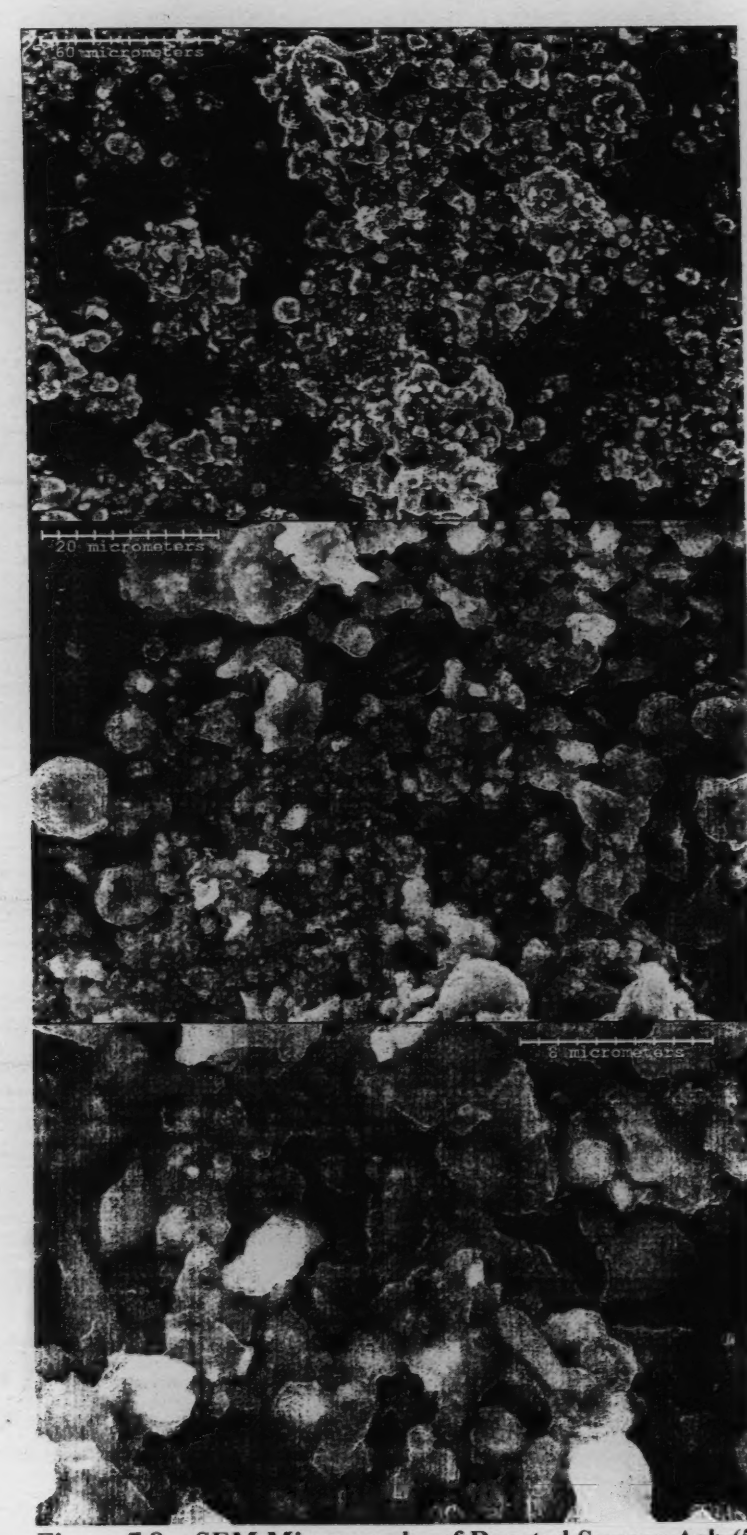


50% Na_2CO_3
500x Magnification

50% Na_2CO_3
1500x Magnification

50% Na_2CO_3
4000x Magnification

Figure 7.7 SEM Micrographs of Roasted Suncor Ash (50% Na_2CO_3, Air Cooled)



50% Na_2CO_3
500x Magnification

50% Na_2CO_3
1500x Magnification

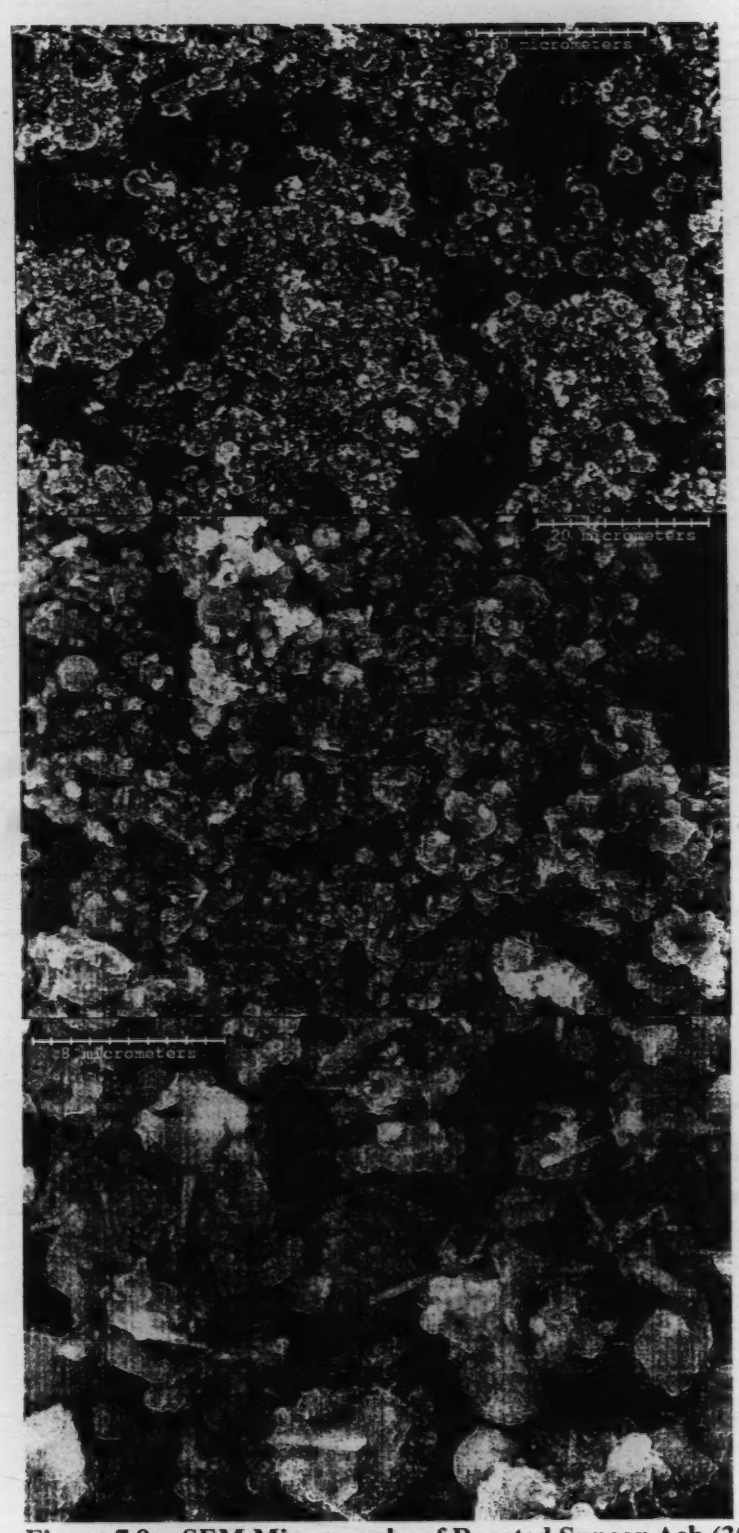
50% Na_2CO_3
4000x Magnification

Figure 7.8 SEM Micrographs of Roasted Suncor Ash (50% Na_2CO_3, Quenched)

7.3.2 Sodium Sulphate

SEM micrographs of fly ash roasted with sodium sulphate are shown in Figure 7.9. The ash roasted with sodium sulphate is visually similar to the ash sample roasted with no reagents. X-ray diffraction confirms this similarity as $Na_2Al_{2x}O_{3x+1}$, a mullite-type structure, cristobalite (SiO_2), hematite (Fe_2O_3) and pseudobrookite (Fe_2TiO_5) are identified as major phases.

Vanadium extractions were actually lower for samples roasted with sodium sulphate, for a given temperature, than samples roasted without the addition of any reagents. The extraction curve (Fig 7.1) is also very flat over a wide range of sodium sulphate additions, indicating that large increases in sodium sulphate additions did little to affect the vanadium extraction. Based on the phases present after roasting and the vanadium extractions observed, it may be concluded that the addition of sodium sulphate had no effect on the phases that crystallized from the ash and a negative effect on the production of water soluble vanadium compounds.



30% Na_2SO_4
500x Magnification

30% Na_2SO_4
1500x Magnification

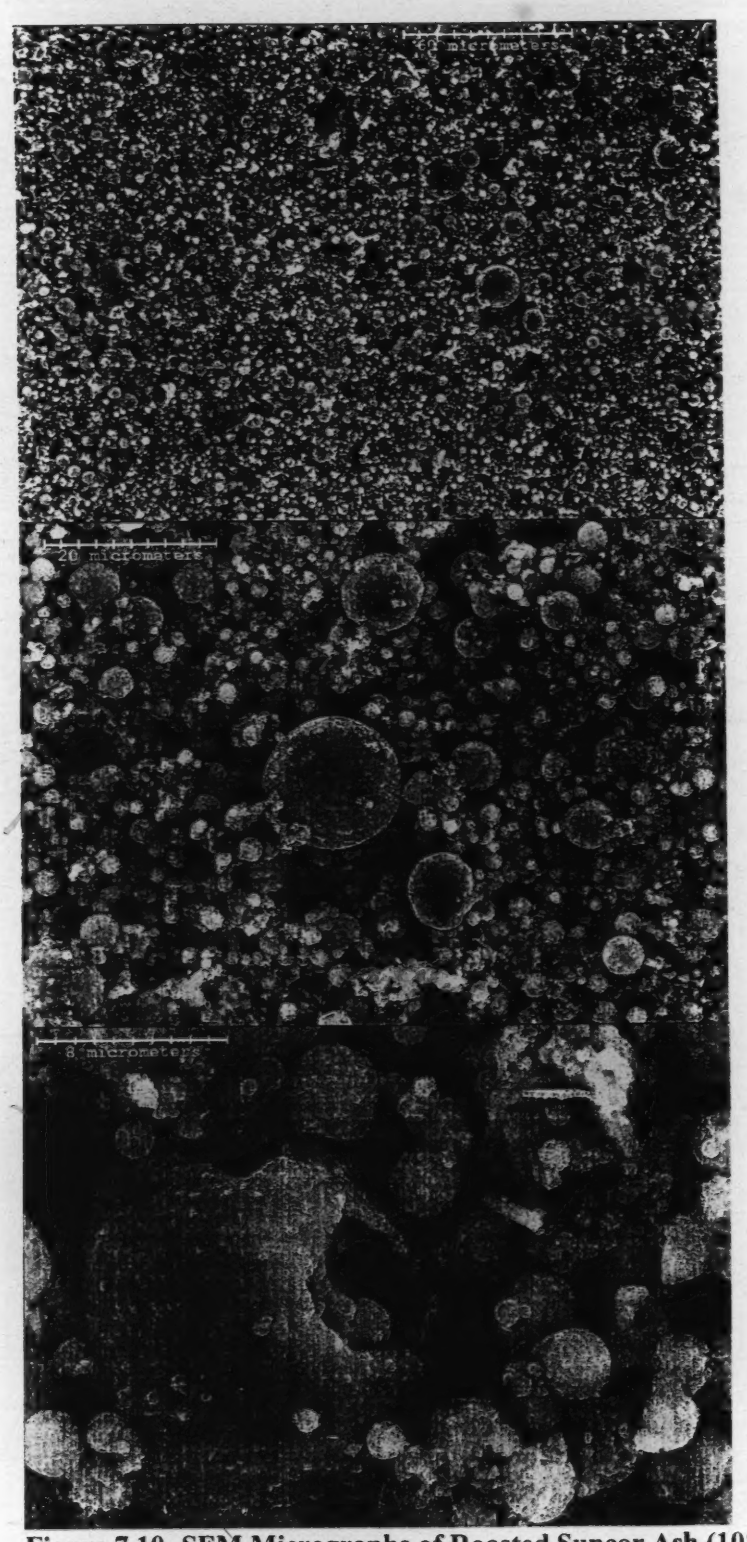
30% Na_2SO_4
4000x Magnification

Figure 7.9 SEM Micrographs of Roasted Suncor Ash (30% Na_2SO_4, Quenched)

7.3.3 Calcium Oxide

Figure 7.10 shows SEM micrographs of fly ash roasted with CaO. Cenospheres remained the predominant structure in the ash roasted with CaO. This is remarkable considering that, with no reagent addition (Section 6.2.1) and the same roasting conditions, the cenospheres decomposed after heating to 850°C for 4h. The addition of CaO appears to react with the glassy matrix to stabilize the cenosphere structure so that they remain stable at higher temperatures.

The x-ray diffraction patterns for the ash roasted with CaO show mostly small broad peaks indicative of a large amount of poorly crystalline material. However, several of the larger peaks would indicate that portions of the ash are beginning to form more crystalline structures as phases, such as cristobalite (SiO_2), hematite (Fe_2O_3) and the mullite type structure, $Na_2Al_{2x}O_{3x+1}$, can be identified. (Though pseudobrookite is not identified as a major phase from XRD, the presence of elongate microcrystals inside of the pleurosphere (hollow cenosphere) at higher magnifications may indicate the presence of minor amounts of pseudobrookite in this sample.) These same phases were documented for the sample roasted with no reagents, but the peaks for that sample were of much higher intensity than observed for the sample roasted with CaO.



10% CaO
500x Magnification

10% CaO
1500x Magnification

10% CaO
4000x Magnification

Figure 7.10 SEM Micrographs of Roasted Suncor Ash (10% CaO, Quenched)

7.3.4 Sodium Nitrate

X-ray diffraction showed a similar group of phases to those formed when roasting with Na_2CO_3, except that nepheline was absent from the observed phases. Cubic feldspathoid minerals, such as noselite ($Na_8Al_6Si_6O_{24}SO_4$) and hauynite ($Na_4Ca_2Al_6Si_6O_{24}SO_4$) are present along with $NiTiO_3$, and possibly Fe_2O_3. However, based on the vanadium extractions achieved, much less water soluble vanadium was produced with roasting with $NaNO_3$.

The lower extractions may be a result of the low melting point of sodium nitrate (306°C) and its low decomposition temperature (~538°C). (Neither Na_2CO_3 nor Na_2SO_4 would be expected to spontaneously decompose to sodium oxide (Na_2O) at the roasting temperatures tested.) As indicated previously for sodium carbonate and sodium sulphate, the extractions for these compounds both decreased when the roasting temperature exceeded the melting point and it may be that roasting with sodium nitrate produces a similar effect. The Na_2O (m.p. =1275°C) formed on decomposition of the sodium nitrate may not be as effective a reagent as Na_2CO_3 in the solid state for producing water soluble vanadium compounds at the temperatures tested.

7.4 Comparison with Previous Testwork

Only one researcher has proposed the use of reagents other than NaCl for alkali roasting of oil sands fly ash. McCorriston (190) indicated that the optimal temperature for vanadium recovery by roasting with sodium carbonate was around 760°C and that a significant drop in vanadium extraction resulted with increased temperature.(189) However, this study indicates that similar vanadium extractions are possible up to 850°C with similar soda additions. McCorriston's tests were conducted without prior removal of carbon from the ash and, based on the detrimental effect of carbon on vanadium extraction (Section 6.2.5) for roasting with NaCl, the decreases in extraction with increasing temperature observed by McCorriston are likely a result of interactions between carbon, soda and vanadium compounds at higher temperatures.

McCorriston's tests with sodium sulphate were conducted on coke and coke ash and the results were poor, with less than 70% extractions reported (191,192) The absence of fly ash from the disclosures in this patent, when compared to her other patents (189,190), is notable as the patent using sodium carbonate as an additive proposed conditions for roasting of fly ash, coke and coke ash. It is suspected that her testwork on roasting fly ash with Na_2SO_4 gave similarly poor results as those observed in this testwork, and, as such, were not reported in the patent application.

7.5 Conclusions

Several roasting reagents, including Na_2CO_3, Na_2SO_4, $NaNO_3$ and CaO, were screened to try to improve the vanadium extractions achieved with salt roasting. Extractions of up to 95% were possible using Na_2CO_3 additions of greater than 50%, while the other reagents did not provide any advantage over roasting with NaCl or, in many cases, over roasting without any reagents. Leaching with 100 g/L H_2SO_4 increased the vanadium extractions, but dissolved large amounts of Al and Si into solution. Leaching with 100 g/L Na_2CO_3 gave only marginal improvements, except for the samples roasted with CaO, where extractions of up to 70% V were reached with only slightly higher levels of impurities dissolved with Na_2CO_3 leaching than with water leaching.

This indicates that Na_2CO_3 could be used as an alternative reagent to NaCl, and could give slightly higher vanadium extractions, but would require higher reagent additions than roasting with NaCl. Roasting with CaO, followed by leaching with Na_2CO_3, was not optimized in this research, but showed promise as relatively high extractions were possible with low reagent additions. Further work would be necessary to determine whether roasting with CaO could be used to give high vanadium extractions.

Characterization with x-ray diffraction and scanning electron microscopy was also used to study the mineralogy and reaction mechanisms associated with these alternative reagents. The table below summarizes the different phases that were formed during roasting with the various reagents tested.

Table 7.1 Summary of Mineral Phases Formed during Roasting of Suncor Ash

Roasting Additive	Minerals Formed during Roasting
No Additives	$Na_2Al_{2x}O_{3x+1}$, cristobalite (SiO_2), pseudobrookite (Fe_2TiO_5).
NaCl	Albite ($NaAlSi_3O_8$), noselite ($Na_8Al_6Si_6O_{24}SO_4$), pseudobrookite (Fe_2TiO_5), hematite (Fe_2O_3)
Na_2CO_3	Nepheline ($(Na,K)AlSiO_4$), noselite ($Na_8Al_6Si_6O_{24}SO_4$), hauynite ($Na_4Ca_2Al_6Si_6O_{24}SO_4$), lazurite ($(Na,Ca)_{4-8}(AlSiO_4)_6(SO_4,Cl)$), $NiTiO_3$, bunsenite (NiO)
Na_2SO_4	$Na_2Al_{2x}O_{3x+1}$, cristobalite (SiO_2), pseudobrookite (Fe_2TiO_5), hematite (Fe_2O_3)
$NaNO_3$	Noselite ($Na_8Al_6Si_6O_{24}SO_4$), hauynite ($Na_4Ca_2Al_6Si_6O_{24}SO_4$), $NiTiO_3$,
CaO	Mostly poorly crystalline; traces of: $Na_2Al_{2x}O_{3x+1}$, cristobalite (SiO_2), hematite (Fe_2O_3)

8.0 Salt Roasting of Syncrude Fly Ash

For a number of reasons, all previous studies have focused on the extraction of metals from Suncor fly ash. First, the volume of ash produced by Syncrude is much lower than for Suncor as a result of the different flowsheets and different strategies for reducing SO_2 emissions used by the two companies. (At Syncrude, bitumen not used in oil production is usually partially burned and stockpiled as coke with only a very small fraction being fully combusted to form fly ash.) Second, the vanadium content of the ash produced by Syncrude is roughly two thirds of the vanadium content of the Suncor ash, on a carbon-free basis, making it a much less attractive material for vanadium recovery.

However, studying the response of the Syncrude fly ash to salt roasting is important as it is likely that any proposed production plant would seek to recover vanadium from the fly ash from both Suncor and Syncrude. As well, understanding the differences in the responses of the two types of ash to salt roasting may provide further information on the reaction mechanisms involved in the salt roasting of oil sands fly ash. Numerous roasting and leaching tests were conducted to determine the effects of various roasting and leaching parameters on vanadium recovery from Syncrude fly ash samples.

8.1 Fly Ash Composition

Three samples from Syncrude were obtained through Syncrude Research. Key chemical analyses of these fly ash samples, after removing carbon and sulphur by roasting at 500°C, are provided in Tables 8.1.

Table 8.1 Syncrude Fly Ash Analyses, wt%

Date	V	Al	Ca	Fe	Mo	Ni	Si	Ti	L.O.I.
Oct 98	2.10	8.19	0.82	8.93	0.24	0.66	21.0	2.24	89.5
Dec 98	1.78	5.87	2.00	3.49	0.13	0.57	36.0	1.17	50.6
2001	2.08	7.43	1.05	14.9	0.20	0.59	20.8	1.75	91.0

Chemical analysis indicated that the composition of the Syncrude ash was much more variable, with Al, Fe and Si ranging from 5.9 to 8.2%, 3.5 to 15.0%, and 21 to 36%,

respectively, and that the carbon content (L.O.I.) of the ash also varied considerably. After removing carbon and sulphur, the Dec 98 ash was quite a dense material, resembling closely the Suncor fly ashes in bulk density, particle size and appearance; the Oct 98 and 2001 samples had very low bulk densities and were much finer and much lighter in color. SEM micrographs of the fly ash samples are shown in Section 3.1.2.2.

8.2 Roasting Tests

8.2.1 Roasting with NaCl

The variability in ash composition is echoed in the response of the fly ash to salt roasting as shown in Figure 8.1. The maximum vanadium extractions from the samples from Oct 1998 and 2001 are in a similar range to Suncor fly ash samples, but require much lower salt additions. The Dec 1998 ash, on the other hand, barely reaches an extraction of 60% V, even at extremely high salt additions.

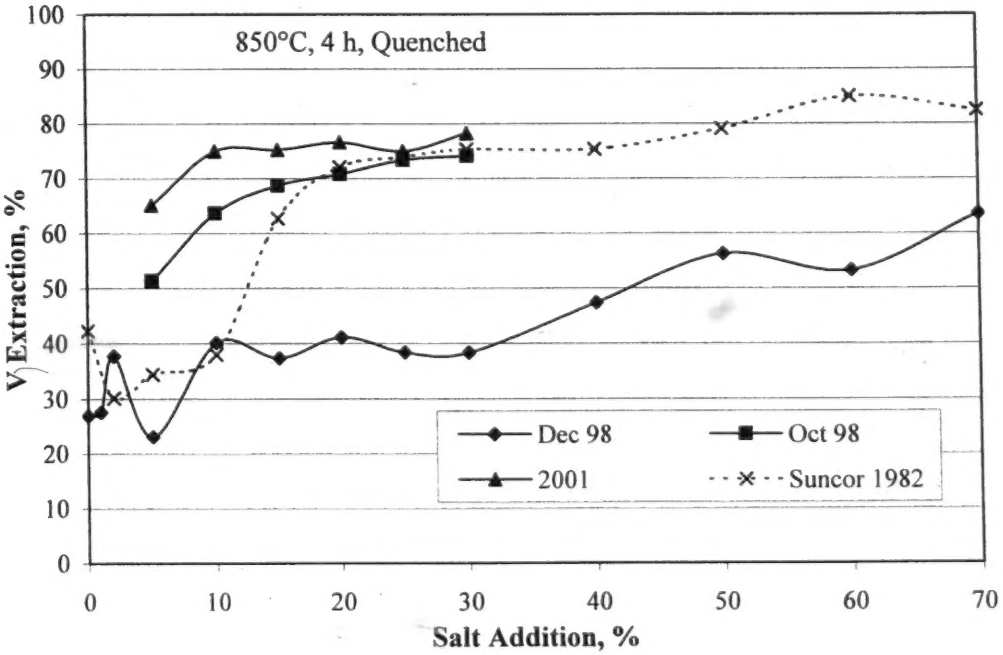


Figure 8.1 Effect of Salt Addition on the Roasting of Syncrude Ash

8.2.1.1 Effect of Roasting Temperature

Similar variability was observed when roasting the three Syncrude ash samples with 20% NaCl at various temperatures. The vanadium extractions for these tests are shown in Figure 8.2.

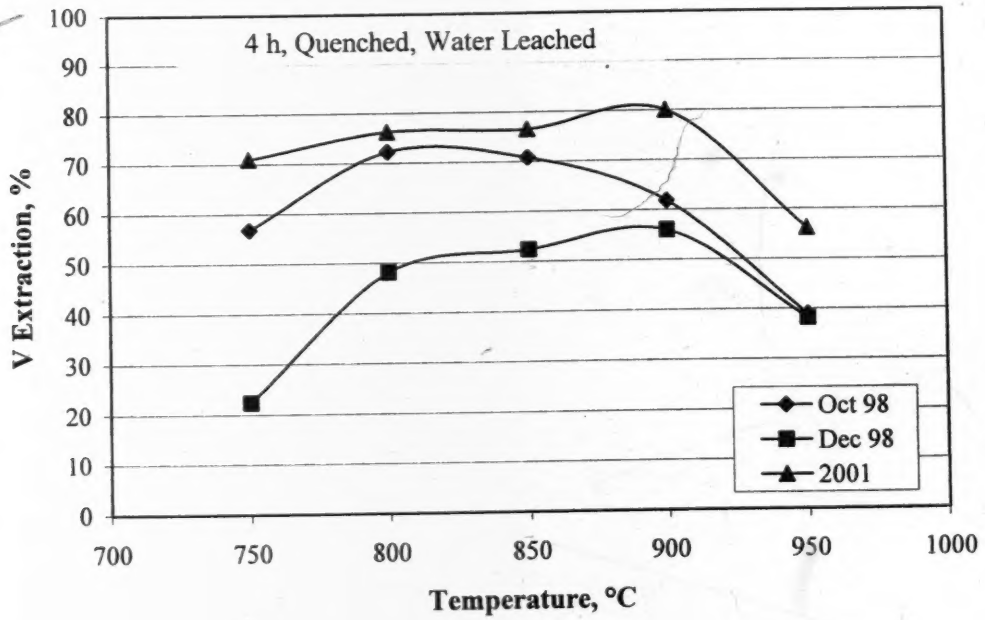


Figure 8.2 Effect of Roasting Temperature on Roasting of Syncrude Ash

The maximum vanadium extraction is much different for each sample (71, 60 and 80% for the Oct 98, Dec 98 and 2001 samples, respectively), and the temperatures where these maximum extractions occur also vary from sample to sample. The Oct 98 sample shows a definite peak in vanadium extraction between 800 and 850°C while the Dec 98 and 2001 samples show maxima at 900°C, and only slightly lower extractions are possible to as low as 800°C. In fact, up to 900°C, the extraction profile for the 2001 ash sample is very flat, with only a 9% difference in vanadium extraction from 750 to 900°C.

Varying the salt addition while roasting the Dec 98 ash at 750 or 950°C showed a similar effect, with slightly lower vanadium extractions at 950°C and much lower vanadium extractions at 750°C, regardless of the salt addition used.

8.2.1.2 Repulp Tests

Due to the poor vanadium extractions from the Dec 98 fly ash, several alternative lixiviants were tested to try to improve the vanadium extraction from the Dec 98 ash and to try to further improve the extractions from the other two samples of Syncrude ash. These reagents included 100 g/L Na_2CO_3, 100 g/L H_2SO_4 and 100 g/L Na_2SO_4. (These ash samples had been roasted with different salt additions and at various temperatures and water leached before being leached with the alternative reagents.)

As shown in Figure 8.3, leaching the Dec 98 fly ash with 100 g/L Na_2CO_3 increased the vanadium extraction to between 75 and 80% while leaching with 100 g/L H_2SO_4 extracted 3 to 7% more vanadium than Na_2CO_3. Acid leaching did increase the amount of Al and Si in solution, compared with water leaching, but the concentrations of Al and Si in the acid leach solution from the Dec 98 sample were at least an order of magnitude lower than similar tests with Suncor ash. Extractions with Na_2CO_3 leaching were similar for Syncrude ash roasted at 950°C (83 to 86%), but were much lower (<56%) for Syncrude ash roasted at 750°C. Higher vanadium extractions were possible with acid leaching (78 to 83% at 750°C and 84 to 90% at 950°C) but with more Al and Si solubilized.

Leaching with sodium carbonate gave more modest improvements of 5 to 10% in the vanadium extraction for the other two Syncrude ash samples. The results of these tests are shown in Figures 8.4 and 8.5. Subsequent testing indicated that leaching the fly ash with 100 g/L Na_2SO_4 solution gave similar vanadium extractions to sodium carbonate leaching. In both cases, the leach solutions contained similar levels of most dissolved impurities, except sodium, to the solutions from the water leach.

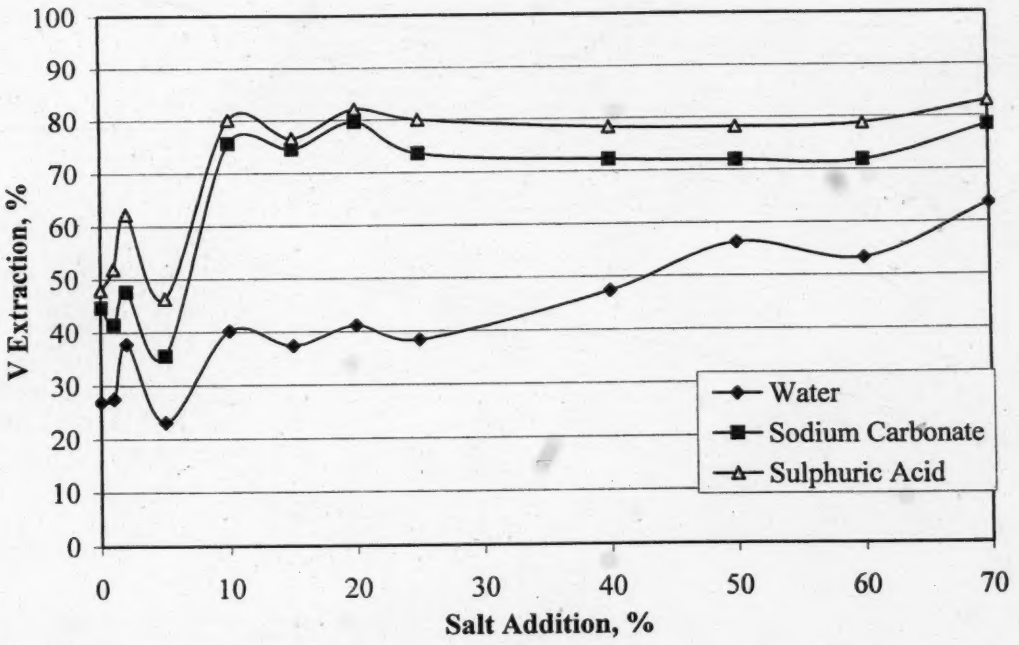


Figure 8.3 Effect of Lixiviant on Vanadium Extraction from Dec 98 Fly Ash

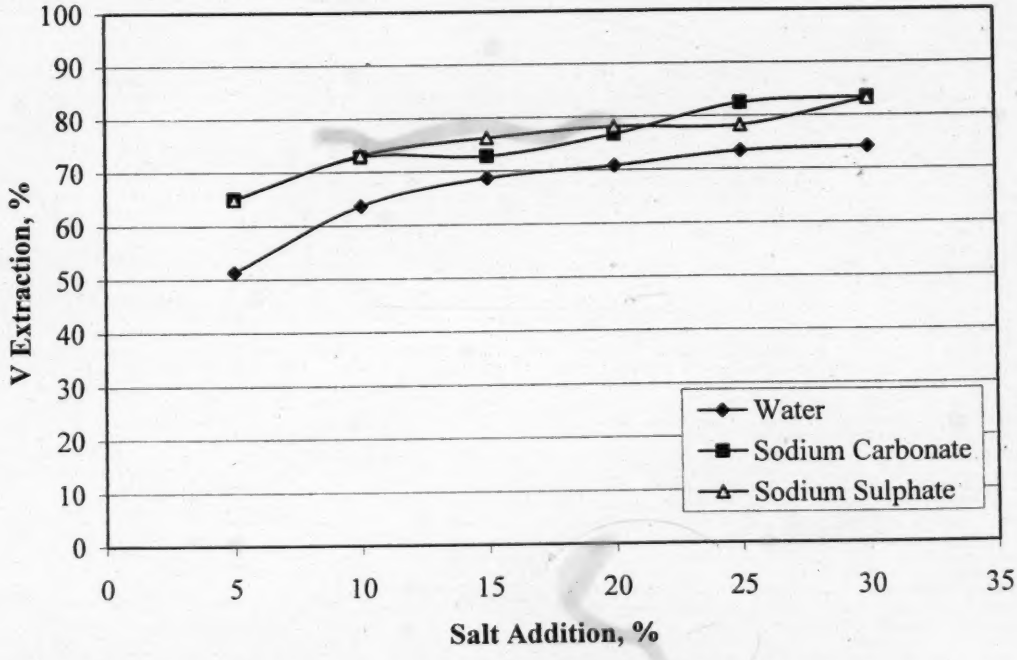


Figure 8.4 Effect of Lixiviant on Vanadium Extraction from Oct 98 Fly Ash

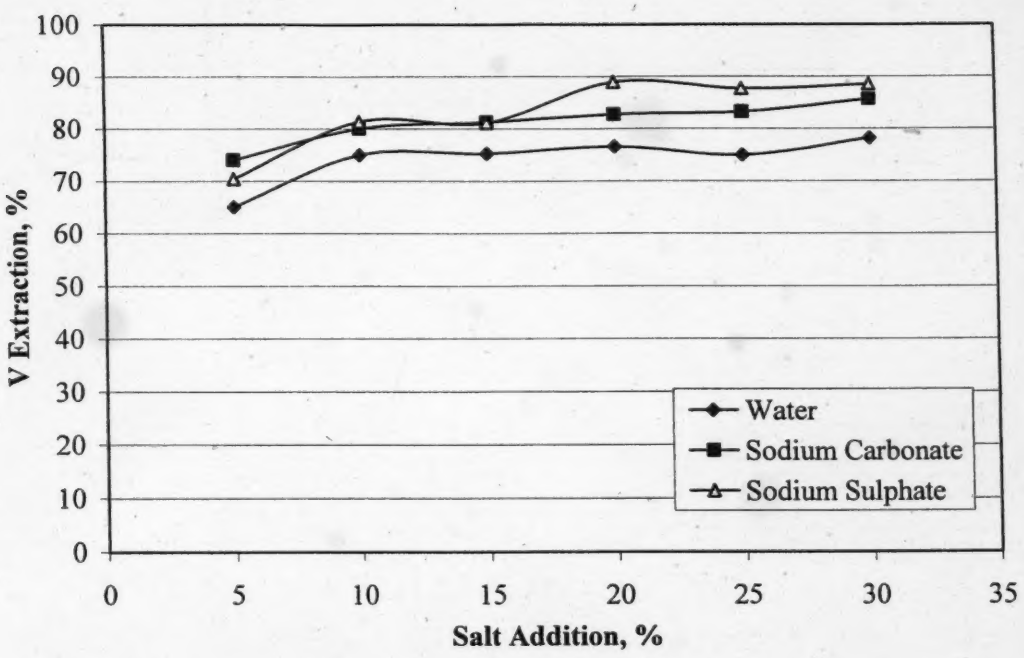


Figure 8.5 Effect of Lixiviant on Vanadium Extraction from 2001 Fly Ash

As expected, quenching the fly ash in sodium carbonate or sodium sulphate solution, instead of in water, followed by leaching in those quench solutions resulted in similar extractions to repulping water leached solids in sodium carbonate or sodium sulphate solutions.

Leaching with sodium carbonate after roasting at different temperatures produced similar improvements in the vanadium extractions. Leaching the Oct 98 and 2001 ash with Na_2CO_3 generally improved the vanadium extractions by 4 to 6%, with slightly higher improvements (9 to 14%) at 750 and 950°C. Maximum vanadium extractions of 77 and 84% were achieved for the Oct 98 and 2001 ashes, respectively, at 800 and 900°C. The increase in vanadium extraction for the Dec 98 ash is more remarkable with between 25 and 40% more vanadium being leached with Na_2CO_3 than with water. The vanadium extraction for the Dec 98 peaked at 900°C with a maximum extraction of 91%.

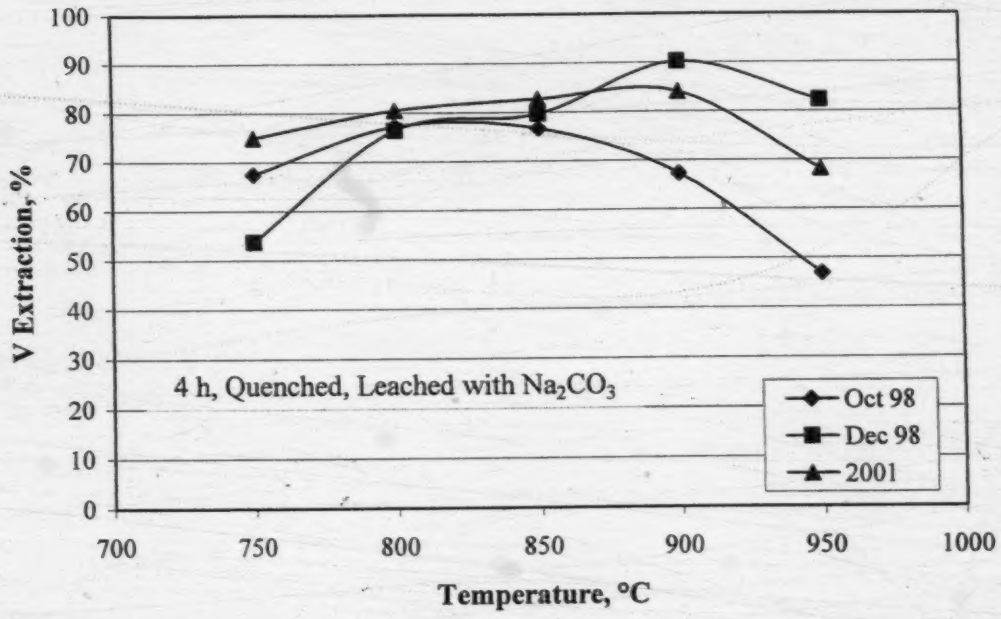


Figure 8.6 Effect of Na_2CO_3 Leaching and Temperature on Vanadium Extraction

Thus, leaching with sodium carbonate or sodium sulphate could be used to improve vanadium extractions from Syncrude fly ash. However, the variability observed in Syncrude fly ash samples makes the selection of optimum roasting conditions challenging. Roasting at a particular set of conditions (e.g. roasting at 900°C instead of 850°C) would, therefore, be expected to give high extractions for some samples and much lower extractions for others, making the Syncrude ash much less desirable as a major feedstock for vanadium production.

8.2.2 Roasting with Sodium Carbonate

Roasting with Na_2CO_3, instead of NaCl, was also unsuccessful in improving the vanadium extraction from the Dec 98 fly ash, as the highest extractions observed were still less than 40%, even at excessively high additions of sodium carbonate. Roasting at 950°C with sodium carbonate further depressed the vanadium extractions, with a maximum extraction of 33% with 15% Na_2CO_3 added.

Leaching these samples with Na_2CO_3 or H_2SO_4 improved the vanadium extractions. The highest vanadium extractions were at soda additions of 10% for samples roasted at 850°C or 950°C, with extractions decreasing steadily at lower or higher soda additions. The maximum extractions with H_2SO_4 were 80% at 850°C and 87% at 950°C, but significant amounts of Al, Fe, Si and Ti were dissolved along with vanadium during leaching. Leaching with Na_2CO_3 was more selective to vanadium and, though extractions were poor from the ash roasted at 850°C with soda (<70%), vanadium extractions with Na_2CO_3 leaching were quite high for ash roasted at 950°C, with extractions only about 5% lower than extractions from acid leaching.

8.2.3 Roasting with No Reagents

For comparison, samples of the Oct 98 and Dec 98 fly ashes were roasted at various temperatures without the addition of any roasting additives. The vanadium extractions from these tests are shown in Figure 8.7.

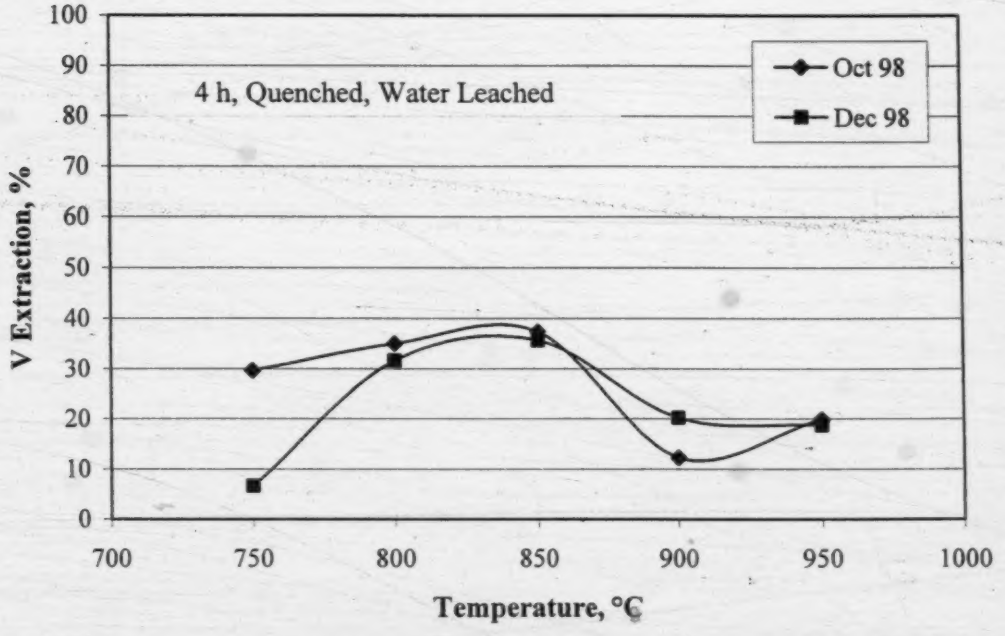


Figure 8.7 Effect of Temperature on Roasting Syncrude Ash with No Additives

Both ash samples show similar trends in vanadium extraction. Maximum extractions are achieved between 800 and 850°C, with a significant drop as the temperature is increased to 900°C and above. The apparent volume of the ash samples, and the Oct 98 ash in particular, which normally have a very low bulk density, decreased significantly with an increase in temperature from 850 to 900°C, producing pellets of roughly one eighth the volume of the original ash samples. It is possible that this significant reduction in apparent volume could be the result of a phase change in the ash, or, perhaps, partial melting of the samples at the higher temperatures.

Leaching these samples with Na_2CO_3 improved the vanadium extractions (Figure 8.8). The Oct 98 ash shows a 10 to 20% improvement in the vanadium extraction and follows the same general trend as the water leaching extraction profile, with a maximum extraction of 49% at 850°C. The Dec 98 ash shows a much different profile, with extractions ranging from 55 to 73%, representing increases of 20 to 45% in the vanadium extraction by leaching with Na_2CO_3. The extraction profile for the Dec 98 ash more closely resembles the profile obtained when roasting that ash with 20% NaCl, but with 12 to 22% lower extractions for most temperatures. Thus, with Na_2CO_3 leaching, relatively high extractions (up to 70%) are possible from the Dec 98 ash, even without using any roasting additives, while roasting with NaCl is critical to obtain high extractions from the Oct 98 ash.

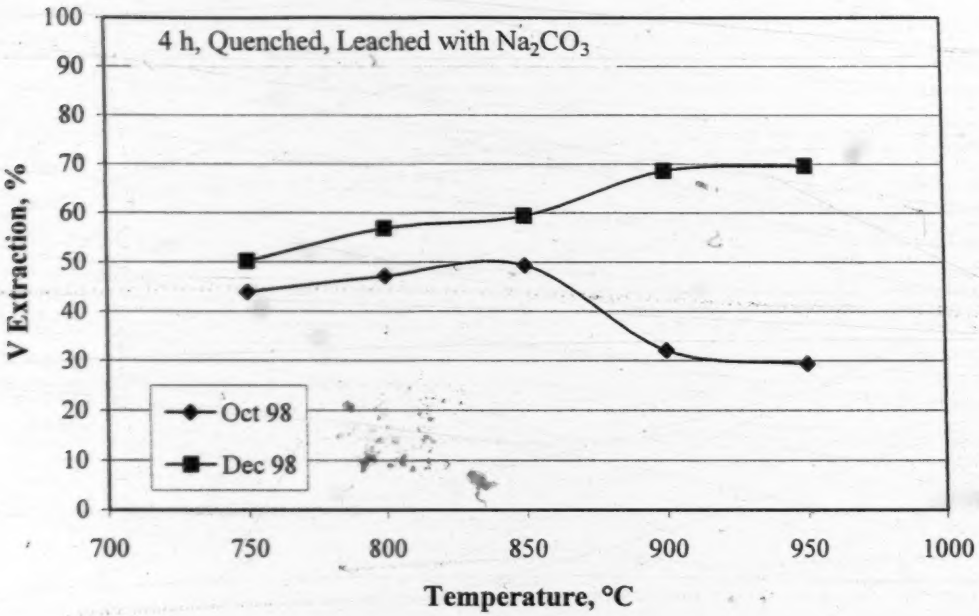


Figure 8.8 Effect of Na_2CO_3 Leaching and Temperature on Vanadium Extraction for Syncrude Ash Roasted without Any Additives

8.2.4 Solution Composition

Overall, water and Na_2CO_3 leaching dissolved only low levels of impurities. Concentrated leach solutions from Syncrude ash were not produced in this testwork, and thus, were not analyzed. However, based on the levels of impurities in the more dilute leach solutions produced in these tests, the projected composition of concentrated leach solutions, assuming that leaching is performed at 50% solids, are shown in the table overleaf.

Table 8.2 Projected Compositions of Concentrated Syncrude Leach Solutions

Ash	Analysis, g/L		Analysis, mg/L				
Sample	V	Mo	Al	Fe	Ni	Si	Ti
Oct 98	10 to 14	0.5 to 0.7	50 to 150	0 to 2	0 to 10	50 to 100	0 to 15
Dec 98	8 to 12	0.4 to 0.6	0 to 15	0 to 20	40 to 60	50 to 100	0 to 10
Jun 01	10 to 14	0.5 to 0.7	50 to 150	0 to 2	0 to 10	50 to 100	0 to 15

8.3 Characterization

8.3.1 Roasted Oct 98 Fly Ash

SEM micrographs for as-received Oct 98 fly ash are provided in Section 3.1.2.2. Before salt roasting, the Oct 98 already has more crystalline phases than the Suncor ash, but still shows significant amounts of poorly crystalline material, as indicated by the numerous broad low intensity peaks in the XRD pattern. Quartz (SiO_2), synthetic hematite (Fe_2O_3), pseudobrookite (Fe_2TiO_5), nickel titanate ($NiTiO_3$), and cristobalite (a high temperature SiO_2 polymorph) were identified as crystalline phases in the unroasted Oct 98 ash sample. (No aluminum or vanadium-bearing phases were identified.)

Roasting at 800 and 900°C with no additives did not change the major phases containing Fe, Ti or Ni, but major peaks for albite ($NaAlSi_3O_8$) could be identified in both samples. The Si:Al mole ratio in the Oct 98 is approximately 2.5:1, or slightly lower depending on the proportion of free quartz, which is closer to the ideal Si:Al ratio for albite of 3:1 than most of the Suncor ashes tested. Thus, on heating, the aluminum and silicon components of the Oct 98 ash along with sodium, and other albite compatible cations, such as K or Ca, appear to crystallize as albite. (The lower Si:Al ratio for the Suncor ash may be the reason why the addition of NaCl is required to promote the formation of an albitic feldspar phase in the roasted ash.) The low concentrations of sodium, and other compatible cations, in the ash, combined with the relatively low vanadium extractions observed, would likely indicate that V^{5+} substitutes partially for Al or Si in the albite structure, as proposed earlier for the Suncor ash in Section 6.4.

After salt roasting the Oct 98 ash, the phases containing Fe, Ti or Ni remain unchanged, but a different aluminosilicate phase is formed. Hauynite ($Na_4Ca_2Al_6Si_6O_{24}SO_4$), which, along with noselite, another cubic feldspathoid phase, was identified in Suncor ash roasted with Na_2CO_3 and $NaNO_3$, is formed with roasted Oct 98 ash in the presence of NaCl. This phase has a much lower (Al+Si):Na ratio than albite (2:1 vs. 3:1 for albite), and, thus, the addition of extra sodium, in the form of NaCl, appears to have promoted the crystallization of this phase instead of a more sodium-poor albitic feldspar phase.

The change in mineralogy was accompanied by an increase in the vanadium extraction from this ash, possibly by the reaction with sodium to form water soluble vanadium compounds or because of a lower vanadium solubility in hauynite than in the feldspar structure.

The high concentration of iron in this ash, relative to the Suncor ash samples or the Dec 98 ash, likely means that most of the iron in the ash is present as Fe_2O_3. (During one session on the SEM, a particle containing Fe and S was identified in the unroasted Oct 98 ash. This phase is presumably pyrite (FeS_2), but was not abundant and, as such, was not identified as a major phase by x-ray diffraction.) It is possible that the high iron content of this ash is due to contamination of the oil sands bitumen with pyrite, which would oxidize to form hematite during coking.

The SEM micrographs of the Oct 98 fly ash after salt roasting (Figures 8.9 to 8.12.) provide little additional information to allow the Oct 98 ash to be further characterized. Overall, the particle size of the roasted Oct 98 ash is very small (often 2 to 4 μm), making it difficult to resolve differences in the structures of the various phases present in the roasted ash. The Oct 98 sample has virtually the same appearance before and after roasting, though the overall particle size in the ash has increased slightly and some microcrystals and large dark grey quartz grains are visible. The elongate crystals observed in the SEM micrographs from all the Oct 98 samples tested were shown to be high in iron and titanium and, as in the Suncor ash, are believed to be the pseudobrookite phase ($FeTi_2O_5$). No structures indicative of the hexagonal structures of hematite or $NiTiO_3$ were identified in the SEM micrographs.

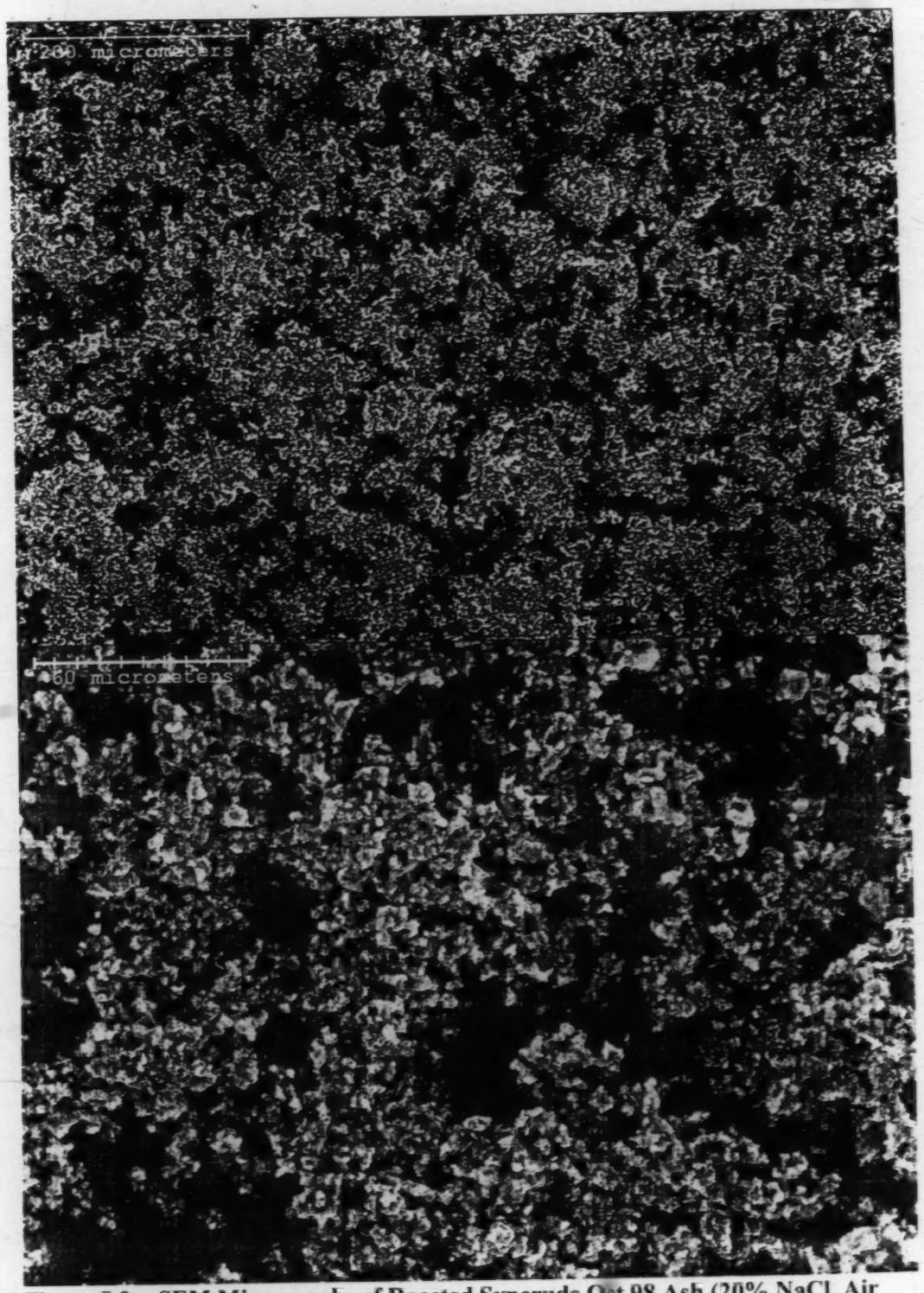


Figure 8.9 SEM Micrographs of Roasted Syncrude Oct 98 Ash (20% NaCl, Air Cooled)

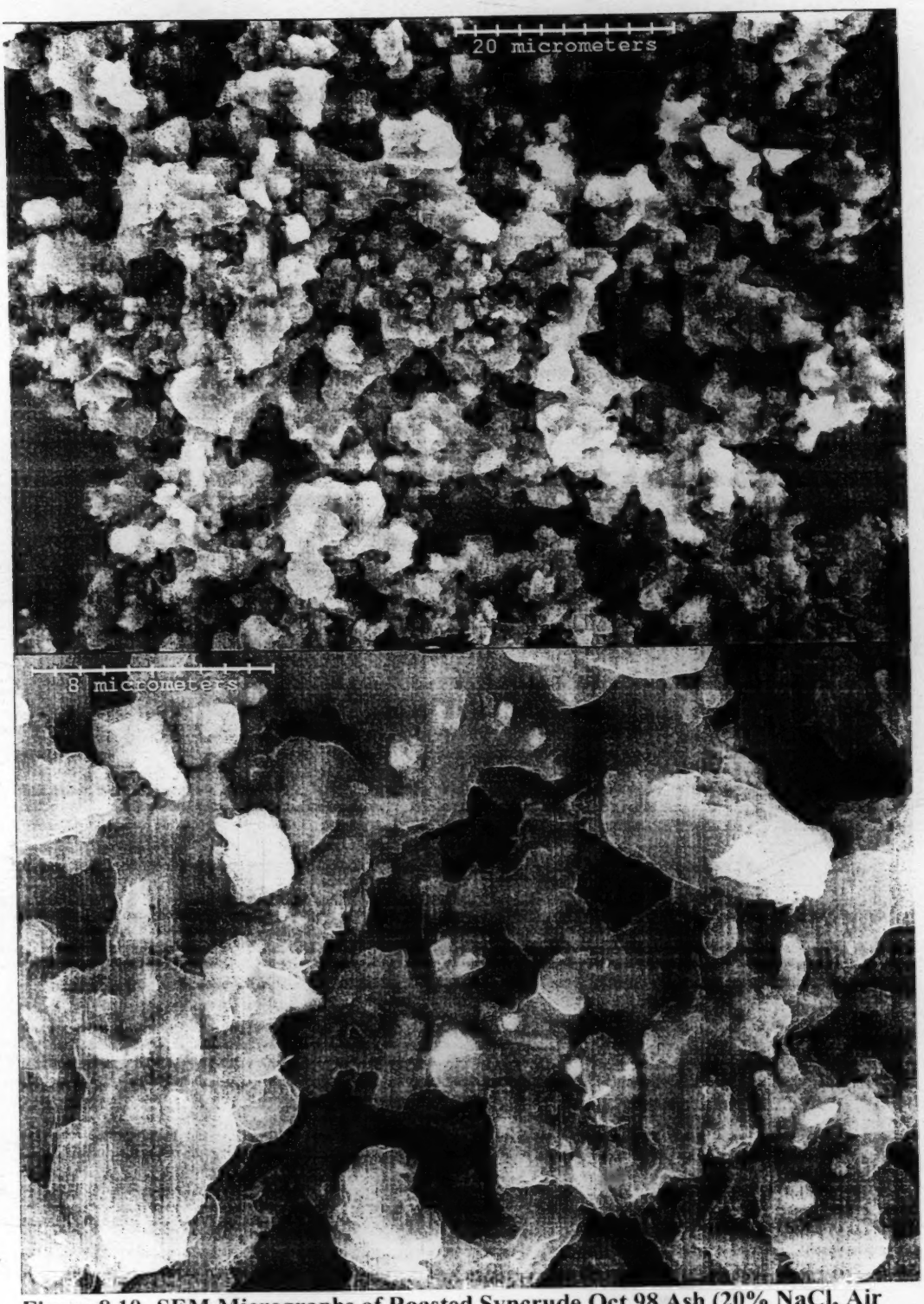


Figure 8.10 SEM Micrographs of Roasted Syncrude Oct 98 Ash (20% NaCl, Air Cooled)

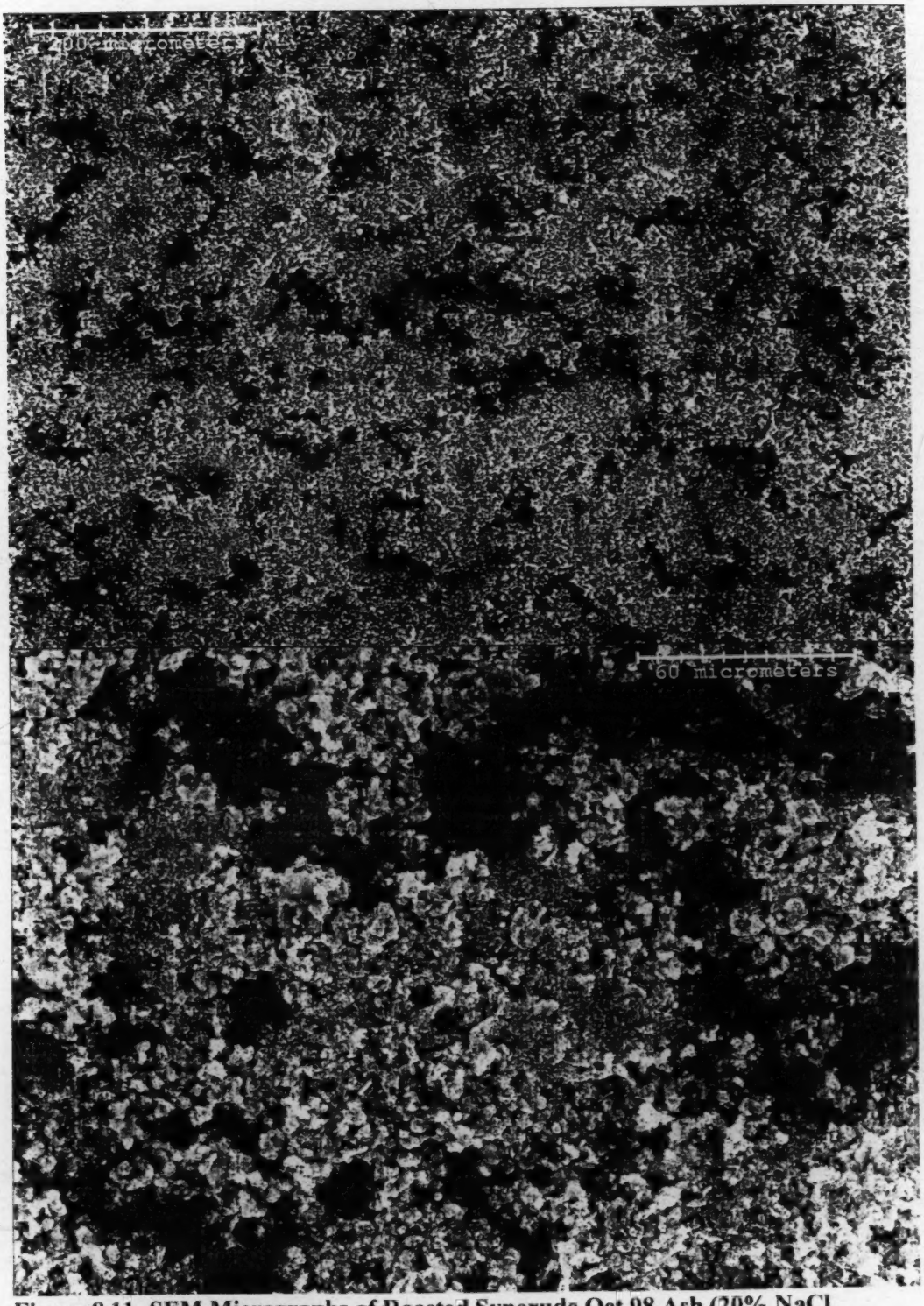


Figure 8.11 SEM Micrographs of Roasted Syncrude Oct 98 Ash (20% NaCl, Quenched)

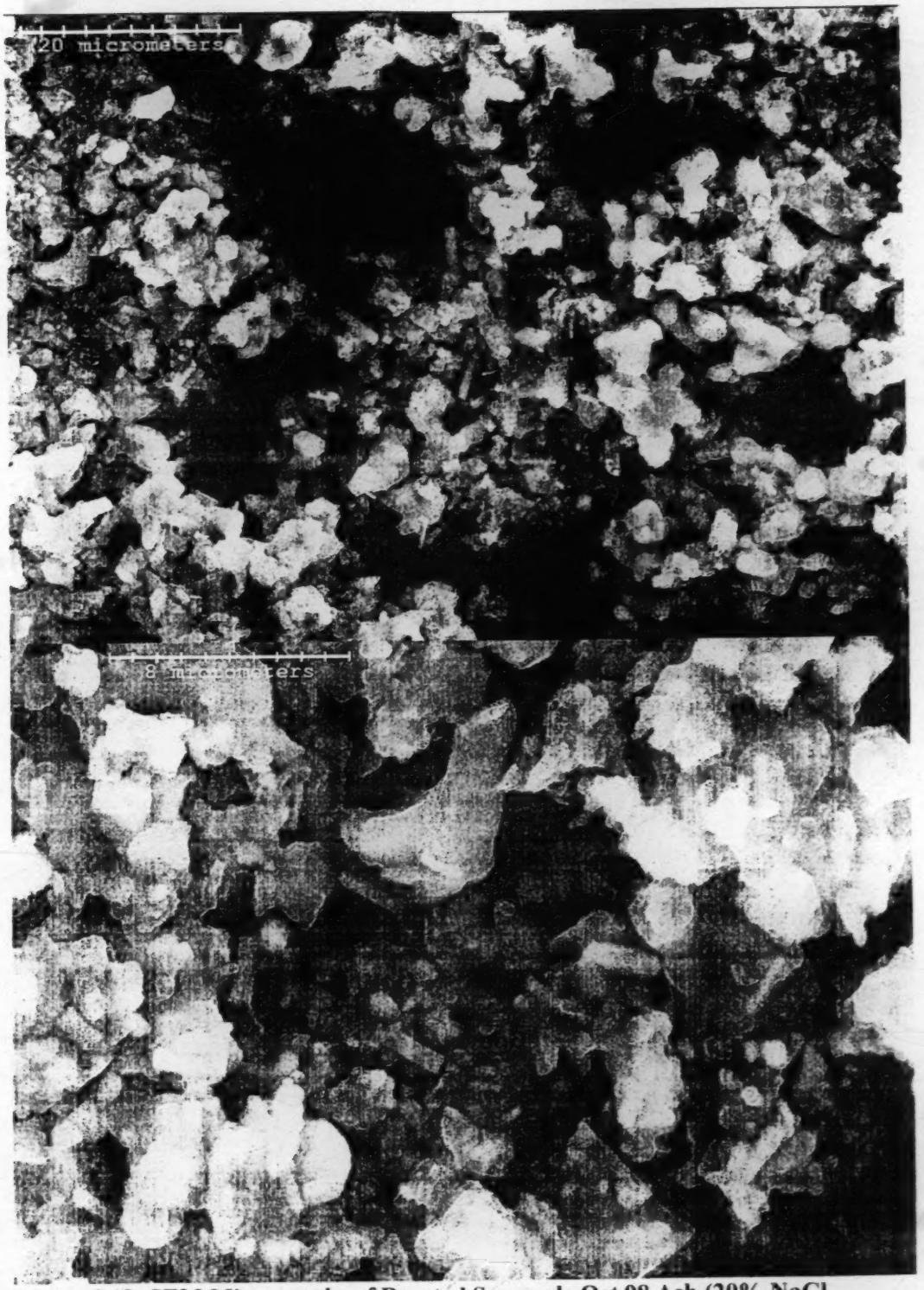


Figure 8.12 SEM Micrographs of Roasted Syncrude Oct 98 Ash (20% NaCl, Quenched)

8.3.2 Roasted Dec 98 Fly Ash

The Dec 98 fly ash proved to be more enigmatic as characterization tests, using the scanning electron microscope and x-ray diffraction, done on this ash sample are much less conclusive than those from the other Suncor and Syncrude ash samples studied.

Before roasting the Dec 98 ash, several structures can be identified in the ash. (SEM micrographs for decarbonized Dec 98 fly ash are provided in Section 3.1.2.2.) Large silica particles (20 to 25 μm), along with microcrystals (0.5 to 1 μm thick), and a few cenospheres (10 to 18 μm), are all visible in the Dec 98. Only quartz (SiO_2) and anhydrite ($CaSO_4$) could be identified as crystalline phases in the Dec 98 ash, though the numerous low intensity peaks observed in the sample mean that a significant amount of poorly crystalline material is present in this sample. In addition, one high intensity peak, at a d-spacing of 1.541, was recorded in the XRD pattern, but could not be identified from available x-ray diffraction patterns. (This peak decreased in intensity after roasting with no additives at 800°C and disappeared when the temperature was increased to 900°C.)

Roasting with no additives at 800°C did not change the major phases that could be identified in the ash, as only quartz and anhydrite were detected in the x-ray diffraction pattern. Anhydrite disappeared from the x-ray pattern when the roasting temperature was increased to 900°C and fewer broad, low intensity peaks were present, indicating a decrease in the amount of poorly crystalline material in the ash. The major peaks for anorthite ($CaAl_2Si_2O_8$), a calcium-rich feldspar, were identified in the 900°C pattern. Thus, it is likely that, at 900°C, the anhydrite and poorly crystalline phases react to form the more crystalline structure of anorthite. Strong quartz peaks are still observed after roasting at 900°C.

These observations, however, do not completely explain the observed behaviour of the Dec 98 fly ash. The Si:Al mole ratio for this ash is nearly 4:1 and, even assuming that nearly 15% of the ash, by weight, is made up of free quartz, the Si:Al ratio of the remaining ash would still be around 3.5:1. This is considerably higher than the 1:1 Si:Al

in the anorthite phase and, even assuming the presence of some albitic, or vanadium-rich, feldspars along with anorthite, the Si:Al ratio, based on these phases, would still be considerably lower than the Si:Al ratio based on the chemical analysis of the ash. (Thus, this likely indicates the presence of additional, unidentified silicate or aluminosilicate phases in this ash.) As well, the high solubility of vanadium from this ash, particularly when leaching with Na_2CO_3, would indicate that a considerable portion of the vanadium in the ash is either present as water soluble sodium vanadium compounds or as reactive vanadium compounds which can be made water soluble by substitution of sodium in their mineral structure. The major x-ray peaks for several compounds, such as potassium dichromate ($K_2Cr_2O_7$) or berlinite ($AlPO_4$), were similar to some of the lower intensity peaks identified from the x-ray patterns for the ash roasted at 900°C; it may be that similar vanadium compounds may be present in the roasted ash, but, as yet, have not been identified or catalogued in available x-ray diffraction data sources.

A slightly different group of phases can be identified from the x-ray patterns for the Dec 98 ash after salt roasting at 850°C. Quartz and anhydrite peaks are still visible, but are much lower in intensity than in the as-received ash or the sample roasted with no additives at 800°C. Major peaks for both anorthitic and albitic feldspars are also identifiable, likely indicating a shift towards the formation of a more sodium-rich feldspar with the additional of NaCl. Iron, titanium and nickel concentrations in the Dec 98 ash are low and, as such, no phase containing Fe, Ni or Ti was identified in the x-ray diffraction patterns of any of the Dec 98 ash samples tested.

Pictures of the salt roasted ash by the scanning electron microscope, however, show a much more remarkable change that would be indicated by the x-ray diffraction patterns. In the air cooled sample, numerous elongate crystals, shown to contain high levels of Fe and Ti by EDX analysis, are visible; some free from the rest of the ash matrix (Figure 8.13) with some fine crystals apparently imbedded within the matrix (Figure 8.14). In the SEM micrographs of the ash sample that had been quenched and water leached (Figures 8.15 to 8.17), a variety of phases with readily distinguishable crystal habits are visible. EDX indicated that the bright structure in the lower left corner

of Figure 8.16 was rich in Ca and V, possibly a calcium vanadate compound. In other portions of the same picture, elongate crystals appear to be imbedded within a platy matrix while small bright, possibly cubic, structures are visible in the upper half of Figure 8.16. Figure 8.17 shows an enlargement of a portion of Figure 8.16 and the platelike structures observed may indicate the presence of an additional hexagonal mineral phase in the roasted ash. Neither large quartz particles nor distinct elongate anhydrite particles, both phases which were identified by x-ray diffraction, were observed by the SEM in either sample.

Thus, based on these differing observations, it is apparent that further study of the Dec 98 ash would be required to be able to more comprehensively understand the mineralogy and reactions taking place during the roasting of this ash. However, as previously mentioned, the presence of cenospheres in this ash, and their absence from the other Syncrude ashes, likely indicates that the Dec 98 ash represents upset conditions in Syncrude's cokers, and, thus, the Dec 98 ash may not be representative of the typical Syncrude fly ash that could be used as feed to a proposed vanadium plant.

However, at the same time, the uniqueness of the Dec 98, even compared with the other oil sands fly ash samples, makes it an extremely interesting material to study from both a technical and mineralogical standpoint. A better understanding of the conditions of the formation of this ash, and its transformations at various temperatures and with the addition of various additives, could lead to a better understanding of the behaviour of various elements and minerals in complex high temperature silicate systems, and possibly even to the identification of previously undiscovered crystalline phases.

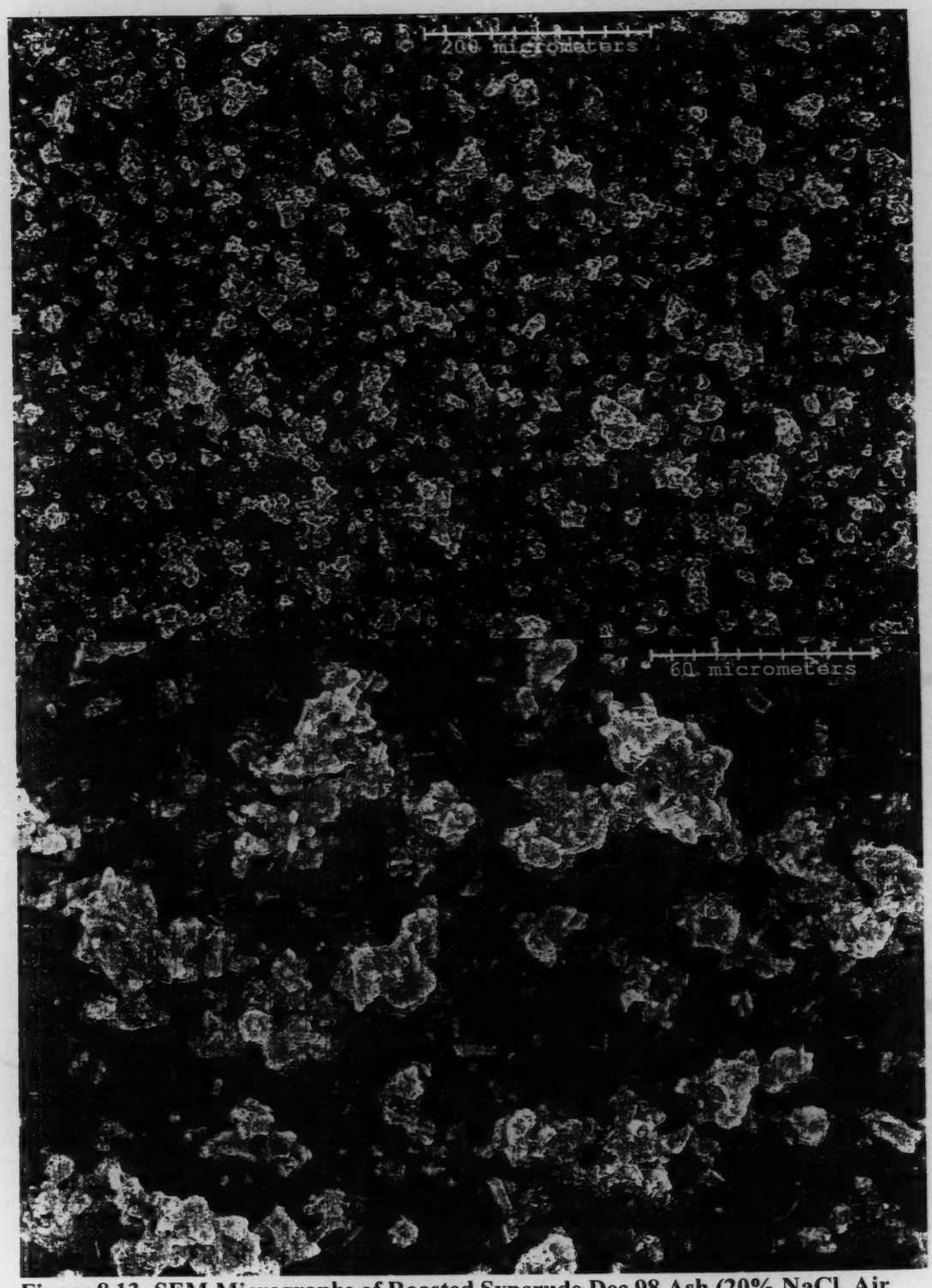


Figure 8.13 SEM Micrographs of Roasted Syncrude Dec 98 Ash (20% NaCl, Air Cooled)

Figure 8.14 SEM Micrographs of Roasted Syncrude Dec 98 Ash (20% NaCl, Air Cooled)

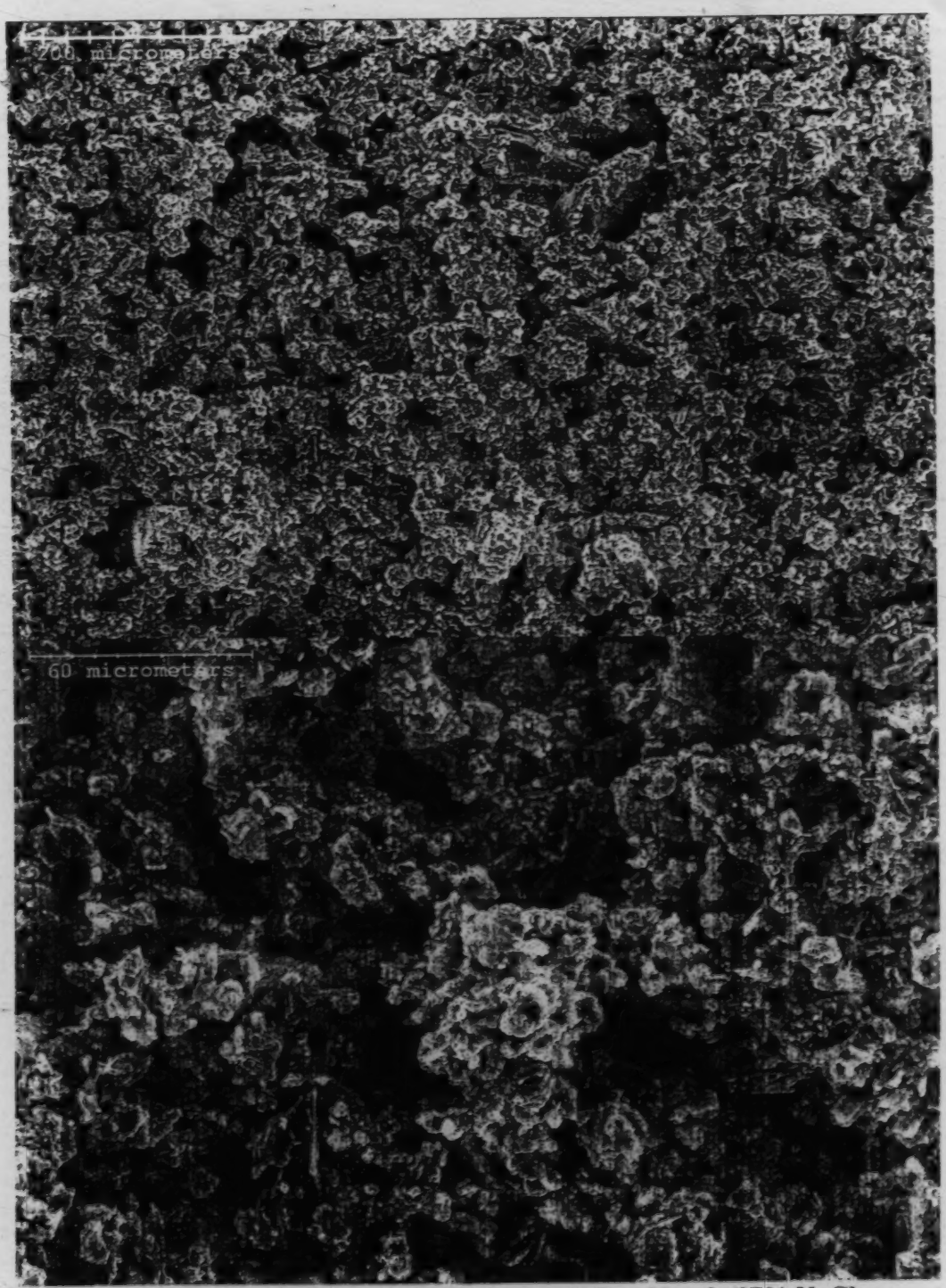


Figure 8.15 SEM Micrographs of Roasted Syncrude Dec 98 Ash (20% NaCl, Quenched) at 150 and 500x Magnification

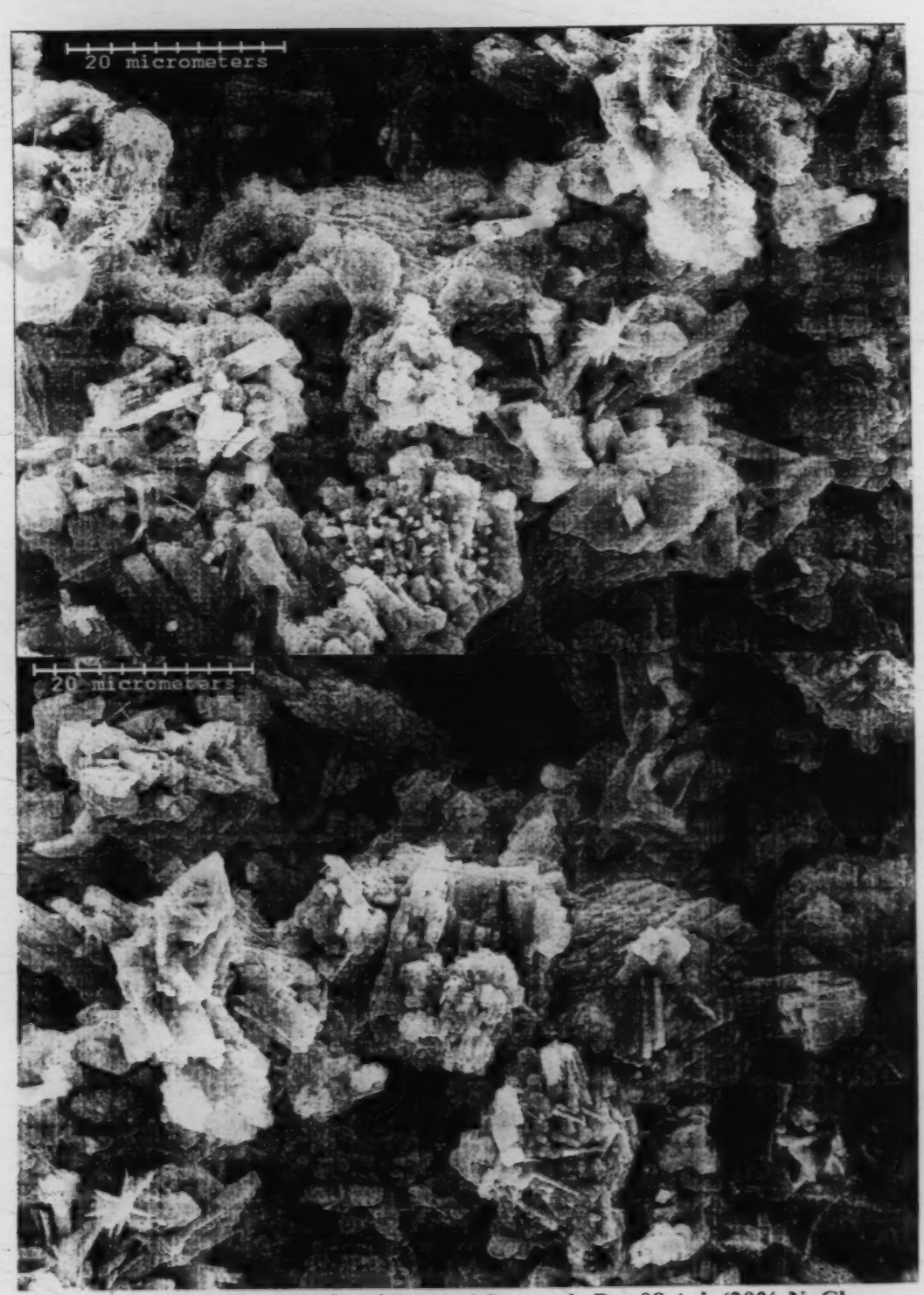


Figure 8.16 SEM Micrographs of Roasted Syncrude Dec 98 Ash (20% NaCl, Quenched) at 1500x Magnification

Figure 8.17 SEM Micrographs of Roasted Syncrude Dec 98 Ash (20% NaCl, Quenched) at 4000x Magnification

8.4 Conclusions

The composition of Syncrude fly ash, and it response to salt roasting varies significantly from sample to sample. As such, optimum roasting conditions cannot be stated definitively for the Syncrude ash, but lie between 800 and 900°C and salt additions of 10 to 25% for all three samples tested. Extractions of less than 80% were possible with water leaching, with less than 60% of the vanadium extracted for the Dec 98 ash with water leaching. Leaching with Na_2CO_3 or Na_2SO_4, on the other hand, increased the vanadium extractions by 5 to 10% for the Oct 98 and 2001 ashes, and increased the vanadium extraction to as high as 80% for the Dec 98 ash sample. Overall, vanadium extractions of 80 to 90% were possible from Syncrude ashes with the use of sodium carbonate leaching, but lower extractions would be expected if conditions proposed for treating Suncor ash were applied to the treatment of Syncrude ash.

The ash samples also showed slightly different responses to changes in roasting temperatures, with higher extractions possible at 900°C for the Dec 98 and 2001 ash samples, than at lower temperatures. Roasting the Dec 98 ash with Na_2CO_3 at 750, 850 or 950°C did not provide any improvements in the amount of vanadium extracted from the ash.

Characterization studies, using the scanning electron microscope and x-ray diffraction, were also conducted to provide insight into the mineralogy of these ashes and the reactions taking place during salt roasting. These tests also showed considerable variation in the fly ash samples tested. Quartz (SiO_2), hematite (Fe_2O_3), pseudobrookite (Fe_2TiO_5), nickel titanate ($NiTiO_3$) and cristobalite (SiO_2) were identified in the as-received Oct 98 ash, with albite ($NaAlSi_3O_8$) forming from poorly crystalline material in the ash on heating with no additives and hauynite ($Na_4Ca_2Al_6Si_6O_{24}SO_4$) forming during salt roasting. In the as-received Dec 98 ash, quartz and anhydrite ($CaSO_4$) were the only identifiable phases, with a significant amount of poorly crystalline material and an unidentifiable crystalline phase also present. On heating to 900°C with no additives, anhydrite and the poorly crystalline phases react to form an anorthitic feldspar

($CaAl_2Si_2O_8$); in salt roasting, anhydrite is only partially decomposed and a combination of albitic and anorthitic feldspars are instead formed from the ash. SEM micrographs of the roasted Dec 98 ash indicate that if is much more complex than initially indicated by the x-ray diffraction analyses, and further study would be required to more accurately characterize this material.

9.0 Vanadium and Molybdenum Recovery from Salt Roast Leach Solutions

A typical leach solution from the Suncor salt-roasting tests contains (mg/L: 12000 to 20000 V, 2 to 35 Al, 5 to 10 Fe, 300 to 600 Mo, 10 to 100 Ni, 40 to 110 Si and 0 to 10 Ti. Molybdenum and nickel extraction in these tests are 30 to 50% and about 1%, respectively, while titanium was relatively inert to salt roasting and water leaching.

Preliminary tests were conducted to determine the feasibility of recovering vanadium from the water leach solutions from salt roasting of oil sands fly ash and to provide information on the precipitation efficiencies and product purities possible using various precipitation flowsheets.

9.1 Background

Historically, vanadium has been precipitated from leach solutions either by acidification to form red cake, which is reported to have a nominal composition of between $Na_2H_2V_6O_{17}$ and $NaH_3V_6O_{17}$, or by the addition of ammonium salts to precipitate ammonium metavanadate (NH_4VO_3) or ammonium polyvanadate ($(NH_4)_2V_6O_{16}$) (19,243,244).

Red cake is precipitated by lowering the pH of the leach solution to about pH 2 and heating the solution to 90 to 97°C. Red cake grades of between 83 to 95% V_2O_5 are reported, but are more routinely in the 83 to 86% range, and can be further upgraded to between 86 and 92% V_2O_5 by calcining at 500°C to produce "black cake" (243,244). Sodium and potassium are normally the major impurities, with the red cake routinely containing between 4 and 11% Na_2O, or K_2O. If present, molybdenum will also precipitate with vanadium, but red cake precipitation is selective to silicon and chromium, which are both common impurities in the solutions produced from salt roasting titanomagnetite ores or slags. One advantage to red cake precipitation is that it can be precipitated efficiently from both dilute (i.e., less than 17 g/L V) and concentrated vanadium solutions (244).

Ammonium metavanadate (AMV), on the other hand, is generally precipitated at room temperature by the addition of either $(NH_4)_2SO_4$ or NH_4Cl. AMV precipitates normally contain around 77% V_2O_5, but can be calcined to produce a V_2O_5 product containing 98 to 99% V_2O_5 (19,243). AMV precipitation is selective to both molybdenum and chromium, which do not form ammonium salts under the same pH conditions (pH 7 to 11), and silicon is generally the major impurity of concern in the ammonium metavanadate precipitates (19). AMV precipitation is generally carried out at high vanadium concentrations (up to 45 g/L V) as these are required for efficient use of the ammonium salts added for the precipitation (19,39). Evaporation of leach solutions is commonly used in industry to increase the vanadium concentration and maximize the efficiency of AMV precipitation (19).

Red cake, and black cake, has been saleable for use in ferrovanadium in the past, as the lower grade and sodium, potassium and molybdenum impurities can be tolerated in ferrovanadium production. However, with the increased use of vanadium in catalysts, nonferrous alloys, and other high purity applications, the higher purity and, specifically, low alkali V_2O_5 product from ammonium metavanadate precipitation has become the most desirable form of vanadium for producers to generate. Although several processes were proposed in the 1960's to metathesize red cake into ammonium metavanadate (243,244), virtually all primary vanadium producers now operate process flowsheets with only ammonium metavanadate or ammonium polyvanadate precipitation. Red cake precipitation may still be practiced commercially, but generally only in situations, such as in uranium production or the treatment of petroleum fly ashes, where acidic lixiviants are involved.

9.2 Red Cake Precipitation

9.2.1 Direct Precipitation

Three scoping tests on direct precipitation of red cake were performed, primarily focusing on the deportment of molybdenum and vanadium during precipitation. The results of these tests are shown in Table 9.1. Precipitation efficiencies were high after 1 h

of precipitation, with precipitation at pH 1.5 being the fastest, followed by precipitation at pH 2 and then pH 1 for all three tests. The precipitate produced was relatively low grade red cake containing only 74 to 82% V_2O_5. In addition, the red cake was contaminated with between 1 and 2% Mo, as molybdenum precipitation was, generally, quite high for these tests.

Rate tests were performed on large batches of concentrated leach solution to determine the dependence of red cake precipitation on reaction time. The results of these tests are shown in Figures 9.1 and 9.2. The rate curves show a similar relationship to that documented in other studies (244), with overall vanadium recovery being strongly related to precipitation time, particularly in the solutions with higher initial vanadium concentrations. In short, more complete precipitation of red cake at faster rates is possible when precipitating red cake from more dilute vanadium solutions; that is, much longer precipitation times would be required to achieve high vanadium precipitations from concentrated leach solutions. This is a significant advantage over ammonium metavanadate precipitation, which often requires evaporation of the leach solution to concentrate and allow efficient precipitation of ammonium metavanadate. It would be expected that red cake precipitation would be possible, even from dilute vanadium-containing waste streams.

The grade of the red cake produced in these precipitation tests was quite variable. The grades of the various red cake precipitates formed are shown in Table 9.2. The grades of the vanadium precipitates in the rate tests were generally quite low, compared with the previous tests where grades of 76 to 82% V_2O_5 were produced, with red cake containing 66, 75 and 56% V_2O_5 produced from precipitation at pH 1.0, 1.5 and 2.0, respectively. The pH with the best precipitation efficiencies (pH 1.5) gave the most consistent red cake grades (74 to 76%). These red cake grades are significant lower than those reported by Schneider (85 to 92%) (39) and somewhat lower than technical grade red cake (83 to 86% V_2O_5) (243).

Table 9.1 Direct Precipitation Scoping Tests

Test 1	Leach Filtrate	Final Solution Analysis, mg/L			Precipitate Analysis, %		
		pH 1	pH 1.5	pH 2	pH 1	pH 1.5	pH 2
Analysis							
Mo	660	2.8	3.3	2.4	n.a.	n.a.	n.a.
V	17100	180	122	95.0	n.a.	n.a.	n.a.
V_2O_5	30400	320	218	169	n.a.	n.a.	n.a.
Precipitation, %							
Mo		95.5	95.9	95.2			
V		88.8	94.1	92.7			
Test 2	Leach Filtrate	Final Solution Analysis, mg/L			Precipitate Analysis, %		
		pH 1	pH 1.5	pH 2	pH 1	pH 1.5	pH 2
Analysis							
Al	n.a.	3.8	4.3	2.5	0.09	0.11	0.06
Fe	n.a.	0.8	0.5	0.2	0.04	0.08	0.07
Mo	600	7.2	3.0	6.1	1.95	1.95	1.82
Ni	n.a.	12.2	15.3	9.6	0.03	0.03	0.04
Si	n.a.	16.2	21.0	13.8	0.25	0.31	0.24
Ti	n.a.	0.3	0.3	0.3	0.1	0.09	0.09
V	18900	386	174	139	45.6	42.8	46
V_2O_5	33600	687	310	247	81.2	76.2	81.9
Precipitation, %							
Mo		89.2	96.1	90.9			
V		81.6	92.8	93.4			
Test 3	Leach Filtrate	Final Solution Analysis, mg/L			Precipitate Analysis, %		
		pH 1	pH 1.5	pH 2	pH 1	pH 1.5	pH 2
Analysis							
Al	9.3	4.2	1.0	0.2	<0.01	<0.01	<0.01
Fe	4.2	2.9	7.5	5.8	0.55	0.63	0.42
Mo	458	6.3	0.4	0.6	0.99	1.05	1.04
Ni	42.9	22.5	5.9	5.8	0.03	0.04	0.03
Si	86.9	41.6	11.8	14.0	<0.01	<0.01	<0.01
Ti	8.1	0.6	0.6	0.7	<0.01	<0.01	<0.01
V	14400	158	45.1	75.9	41.3	42.4	42.9
V_2O_5	25600	282	80	135	73.5	75.5	76.4
Precipitation, %							
Mo		96.9	99.5	99.2			
V		97.5	98.0	96.7			

*Leach extractions were 75.1, 74.8 and 74.5% for Tests 1, 2 and 3, respectively.

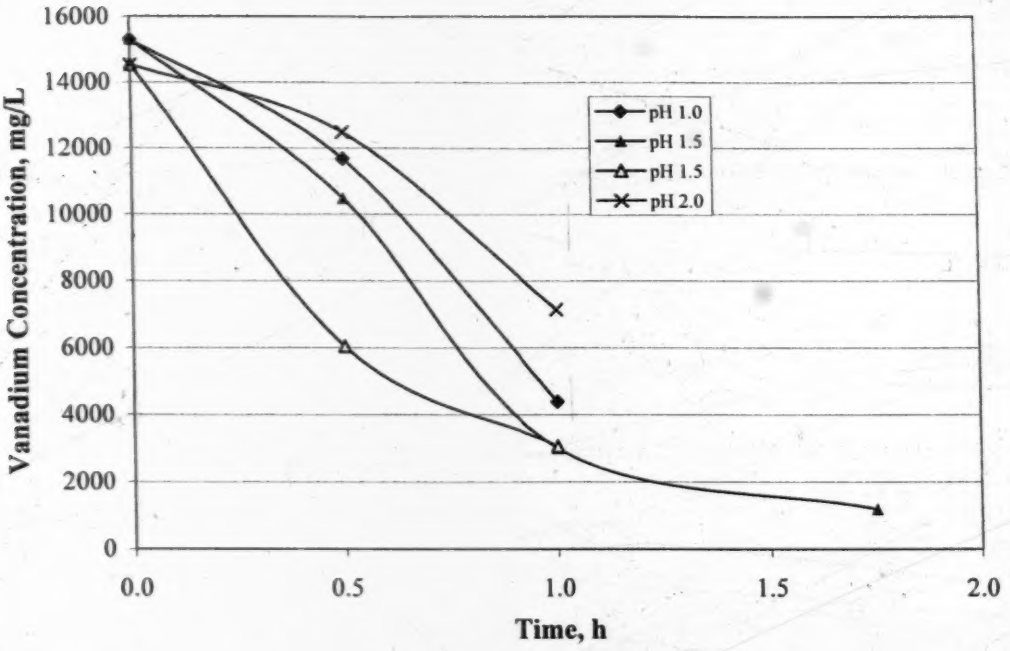


Figure 9.1 Vanadium Concentration versus Time for Red Cake Precipitation[a,b]

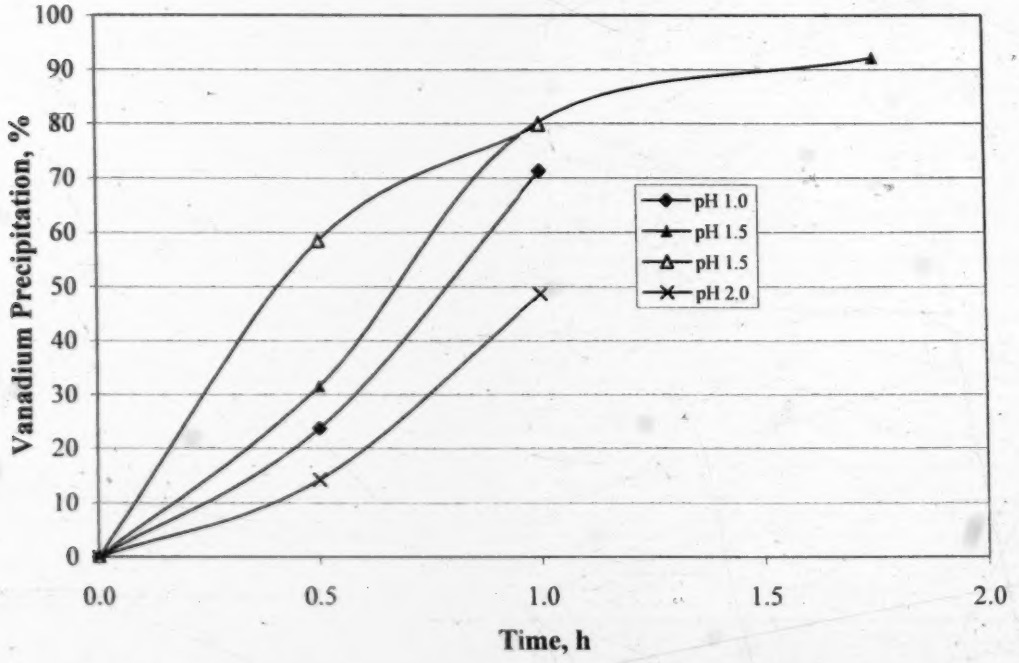


Figure 9.2 Precipitation Efficiency versus Time for Red Cake Precipitation

[a] The vanadium concentration at 0.5 h for the precipitation at pH 1.0 was estimated based on available data.
[b] Two tests were performed at pH 1.5 for different total precipitation times.

Table 9.2 Composition of Red Cake Samples from Direct Precipitation

	Scoping Tests						Rate Tests			
	Test 2			Test 3						
	pH 1.0	pH 1.5	pH 2.0	pH 1.0	pH 1.5	pH 2.0	pH 1.0	pH 1.5	pH 1.5	pH 2.0
Analysis										
Al, %	0.09	0.11	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	0.04	0.08	0.07	0.55	0.63	0.42	<0.01	<0.01	<0.01	<0.01
Mo	1.95	1.95	1.82	0.99	1.05	1.04	1.17	1.00	0.88	0.85
Ni	0.03	0.03	0.04	0.03	0.04	0.03	0.04	0.04	<0.01	<0.01
K	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.15	0.15	0.07	0.18
Si	0.25	0.31	0.24	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.01	0.69	0.19	0.67
Ti	0.1	0.09	0.09	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
V	45.6	42.8	46.0	41.3	42.4	42.9	37.2	42.6	41.6	31.0
V_2O_5	81.2	76.2	81.9	73.5	75.5	76.4	66.2	75.8	74.0	55.2

The variability of the vanadium grade from test to test would be troublesome, as it may be difficult to ensure that a high grade red cake product can be produced. As well, the contamination of these precipitates with Mo and Na could make these precipitates less marketable as a final vanadium product, thereby requiring further solution purification, such as solvent extraction, before precipitating vanadium.

Some red cake samples were calcined at 500°C to produce "black cake". This generally improved the grade of the vanadium precipitates by 8 to 10%, with a maximum grade of 84% V_2O_5 measured for the samples roasted to form black cake.

9.2.1.1 Detailed Analyses of Solutions and Solids

Detailed analyses of major and minor elements for the leach and precipitation solutions from Test 3 are shown in Table 9.3. Another sample of leach solution was analyzed and was found to contain around 10 g/L Na and 3.2 g/L K.

Table 9.3 Detailed Analysis of Leach and Direct Precipitation Solutions and Solids

	Solution Analysis, mg/L					Solids Analysis, %		
	Leach		Precipitation*			Precipitation		
	Filtrate	Wash	pH 1.0	pH 1.5	pH 2.0	pH 1.0	pH 1.5	pH 2.0
Analysis								
Al	9.3	1.2	9.6	6.2	1.3	<0.01	<0.01	<0.01
Cd	9.4	0.5	10.3	11.0	11.1	<0.01	<0.01	<0.01
Ca	662	394	352	636	613	0.59	0.52	0.46
Cr	0.9	0.8	1.7	3.8	3.0	0.03	0.04	0.03
Co	8.1	1.6	14.8	13.1	12.4	<0.01	<0.01	<0.01
Cu	0.9	0.1	1.8	1.9	1.0	0.003	0.003	0.004
Fe	4.2	<0.1	6.6	46.6	36.5	0.55	0.63	0.42
Pb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01	<0.01
Mg	73.1	24.2	n.a.	n.a.	n.a.	0.83	0.76	0.79
Mn	248	21.9	245	204	174	0.08	0.17	0.10
Mo	458	34.2	14.4	2.5	3.8	0.99	1.05	1.04
Ni	42.9	5.7	51.3	37.1	36.5	0.03	0.04	0.03
Si	86.9	9.7	94.8	73.6	88.5	<0.01	<0.01	<0.01
Ag	31.0	0.7	14.7	7.6	6.5	0.02	0.02	0.02
Ti	8.1	13.0	1.4	3.7	4.4	<0.01	<0.01	<0.01
V	14400	1410	361	281	480	41.3	42.4	42.9
V_2O_5	25600	2510	643	501	854	73.5	75.5	76.4
Zn	16.2	1.2	9.7	19.9	24.3	0.01	0.01	0.02

* Corrected for evaporation/dilution

Magnesium, calcium, iron and molybdenum, and, from analysis of other samples, sodium, are the majority impurities in the red cake produced, with concentrations ranging from 0.4 to 1.1%. Precipitation of most other impurities in the red cake is either low or negligible, even for elements such as Mn, which were present in high concentrations in the leach solutions.

9.2.2 Molybdenum Removal and Precipitation

Further scoping tests were performed to determine whether a process could be developed to selectively remove molybdenum from the leach solution prior to precipitating red cake and, thus, produce a vanadium-free red cake precipitate and a possibly saleable

molybdenum product. Several different flowsheets were tested, including precipitation of molybdenum as an oxide and as a sulphide in acidic solution. The most successful method for molybdenum removal is shown in Figure 9.3.

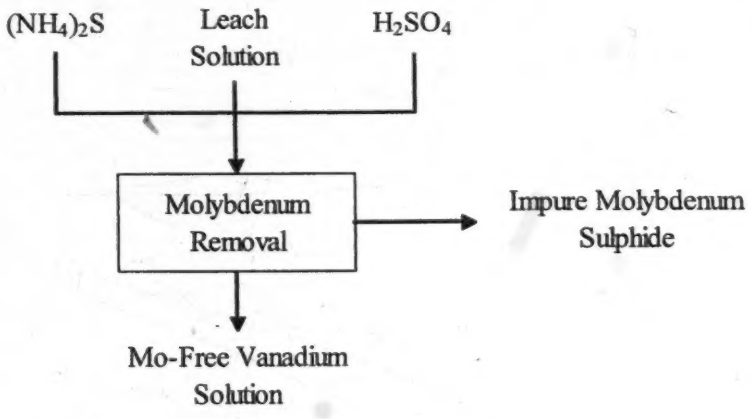


Figure 9.3 Molybdenum Removal Process

Acid is added to adjust the leach solution to pH 1 at room temperature and $(NH_4)_2S$ is then added to precipitate Mo, and some Ni, as insoluble sulphides. Generally, three cycles of acidification and sulphidation were required to lower the molybdenum to less than 10 mg/L in the solution, with the pH cycling between pH 1 and 3 in each cycle. (The completion of the molybdenum precipitation reaction is generally noted by the formation of bubbles (H_2S) at the surface of the solution on the addition of further $(NH_4)_2S$.) Vanadium also reacts with $(NH_4)_2S$ to form V^{4+} during molybdenum removal, giving a characteristically blue V^{4+} solution. Thus, before vanadium could be precipitated as red cake, the addition of sodium chlorate was required to oxidize the vanadium in the resulting solution from V^{4+} to V^{5+}.

Three tests were performed to test the molybdenum removal flowsheet. The results of the molybdenum removal tests are shown in Tables 9.4 to 9.7.

Table 9.4 Molybdenum Removal Test 1

	Solution Analyses, mg/L				Precipitate Analysis, %			
	Leach Filtrate	Mo Removal	Precip. Filtrate		Vanadium		Molybdenum	
			Mo-Free	Direct	Mo-Free	Direct	Unroasted	Roasted
Analysis								
Al	19.9	10.9	16.7	14.6	0.06	0.03	0.02	0.09
Fe	9.5	7.0	4.8	1.3	0.06	0.05	0.04	0.17
Mo	540	2.1	0.6	34.0	0.06	1.81	1.16	4.94
Ni	58.0	11.8	14.8	39.4	0.04	0.04	0.07	0.32
Si	73.4	43.9	58.8	71.5	0.25	0.33	0.04	0.19
Ti	10.3	8.8	1.8	0.2	0.10	0.13	0.00	0.01
V	13200	6780	224	530	44.4	46.8	1.27	5.42
V_2O_5	23400	12100	399	943	79.0	83.3	2.26	9.65
Extraction, %	72.8							
Precipitation, %								
Mo		99.1	99.7*	88.1				
Ni		61.7	66.5*	15.5				
V		5.9	94.5*	89.8				

* Cumulative precipitation in molybdenum removal and vanadium precipitation

Table 9.5 Molybdenum Removal Test 2

	Solution Analyses, mg/L				Precipitate Analysis, %	
	Leach Filtrate	Mo Removal	Precipitation Filtrate			
			Mo-Free	Direct	Mo Free	Direct
Analysis						
Al	9.3	5.7	24.2	1.0	<0.01	<0.01
Fe	4.2	3.5	2.4	7.5	0.37	0.63
Mo	458	1.7	<0.1	0.4	0.06	1.05
Ni	42.9	7.0	4.6	5.9	0.04	0.04
Si	86.9	37.7	22.6	11.8	<0.01	<0.01
Ti	8.1	5.0	0.0	0.6	<0.01	<0.01
V	14400	6790	137	45.1	38.8	42.4
V_2O_5	25600	12100	243	80.3	69.1	75.5
Extraction, %	72.8					
Precipitation, %						
Mo		99.3	>99.9*	99.5		
Ni		69.9	69.9*	14.2		
V		11.5	97.0*	98.0		

* Cumulative precipitation in molybdenum removal and vanadium precipitation

Table 9.6 Solution Analyses for Molybdenum Removal Test 3

	Solution Analyses			
	Leach Filtrate	Mo Removal	Precipitation Filtrate	
			pH 1.5	pH 2.0
Analysis, mg/L				
Al	5.0	4.2	1.2	2.7
Fe	3.6	2.4	0.4	0.4
Mo	338	8.5	0.5	0.6
Ni	29.9	4.8	3.6	3.6
Si	98.0	64.0	52.0	51.0
Ti	4.8	4.2	<0.1	<0.1
V	14400	10300	107	106
V_2O_5	25600	18400	190	189
Leach Extraction, %	73.5			
Overall Precipitation, %				
Mo		96.2	3.6	3.5
Ni		76.7	5.9	5.7
V		0.2	98.8	98.8

Table 9.7 Solids Analyses for Molybdenum Removal Test 3

	Precipitate Analysis, %					
	Mo Removal		Orange Cake		Roasted Cake	
	Unroasted	Roasted	pH 1.5	pH 2.0	pH 1.5	pH 2.0
Analysis, %						
Al	0.12	0.89	<0.01	<0.01	0.05	0.06
Fe	0.05	0.42	<0.01	<0.01	<0.01	<0.01
Mo	2.01	15.5	0.07	0.07	0.06	0.06
Ni	0.14	1.05	<0.01	<0.01	<0.01	<0.01
K	n.a.	n.a.	0.16	0.1	<0.01	<0.01
Si	0.04	0.32	<0.01	<0.01	0.05	0.09
Na	n.a.	n.a.	<0.01	<0.01	0.17	0.15
Ti	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
V	3.0	23.3	41.0	43.0	46.4	47.2
V_2O_5	5.4	41.4	73.0	76.5	82.6	84.0
Wt. Loss, %		83.8			12.3	9.5

* Corrected for evaporation/dilution

Molybdenum precipitation was rapid with greater than 99% of the molybdenum in solution precipitated in the first two tests, with a slightly lower molybdenum precipitation of 96% in Test 3. This lowered the molybdenum in the leach solution from between 340 and 540 mg/L to between 1.7 and 8.5 mg/L. A significant excess of $(NH_4)_2S$ was required to precipitate molybdenum under these conditions. (Test 1 required an excess of about 20 times, while refinement to the additions in subsequent tests lowered the required excess to between 8.6 and 9.2 times stoichiometric.) This high addition is not unexpected as precipitation with sulphides at low pH would be expected to produce a significant portion of S° and polysulphides, due to reaction of S^{2-} ions with H^+ ions in solution.

The high additions of $(NH_4)_2S$ result in a relatively impure molybdenum sulphide product, with molybdenum grades of only 1 to 2%. Roasting at 600°C resulted in weight losses of 77 to 84%, indicating that much of the precipitate is made up of elemental sulphur and sulphide sulphur. Roasting increased the molybdenum grade in the precipitate to 5% for Test 1 and up to 15.5% for Test 3.

Between 61 and 77% of the nickel in the leach was also precipitated, presumably as a nickel sulphide, along with molybdenum, with nickel concentrations in the roasted precipitate ranging from 0.3 to 1.1%. Some vanadium is also precipitated during molybdenum removal, corresponding to vanadium losses to the molybdenum precipitate of between 0.2 and 11.5%. The vanadium grade of the molybdenum precipitate varies from 5.4% for Test 1 to up to 23.3% for Test 3.

Vanadium was oxidized from V^{4+} to V^{5+} with $NaClO_3$, after molybdenum precipitation was complete. The oxidation process is relatively slow, compared with molybdenum precipitation; even with an excess of 2.7 to 6.0 times $NaClO_3$ added, up to 20 minutes were required to fully oxidize vanadium to V^{5+}. Monitoring of the solution potential indicated that solution potentials of between 1250 and 1300 mV were easily reached with $NaClO_3$, but, though more than oxidizing enough to oxidize vanadium, these potentials did not guarantee quick oxidation of the vanadium to V^{5+}. In Test 3, in particular, additions of $NaClO_3$ to the solution, once an ORP of 1250 mV was reached, produced a murky green solution with a bad odor, possibly as the result of the oxidation of Cl^- ions to Cl_2 by excess $NaClO_3$. (In one scoping test, excessively high $NaClO_3$ additions and, apparently, the subsequent stripping of Cl^- from the solution, led to the formation of a vanadium precipitate contaminated with between 8.5 and 9.7% Na.) In another scoping test, similar difficulties in oxidizing the solution were encountered when $KMnO_4$ was used as the oxidizing agent. Although the Petrofina refinery was successful in oxidizing V^{4+} solutions to V^{5+} (195), other producers indicate difficulties in controlling the vanadium oxidation reaction when using $NaClO_3$ as the oxidant (245). Further research would be required to improve the oxidation of vanadium in molybdenum removal solution before such a process could be used commercially.

Precipitation of vanadium from the oxidized molybdenum removal solution at pH 1.5 resulted in the rapid formation of red shot-like particles from the solutions from Tests 1 and 2. (Red cake was also precipitated directly from the leach solution, without molybdenum removal, in these two tests for comparison.) Between 94 and 97% of the vanadium in the oxidized molybdenum removal solution was precipitated in Tests 1

and 2. This compares with precipitation efficiencies with direct precipitation of 90 and 98% in Tests 1 and 2, respectively. Due to the vanadium losses during molybdenum removal, the vanadium recovery, as a percentage of the vanadium in the original leach solution, was either similar (Test 1) or significantly higher for direct precipitation than for precipitation after molybdenum removal.

Molybdenum free red cake was successfully precipitated after the molybdenum removal step, though the grades of the precipitate (79% and 69% V_2O_5 for Tests 1 and 2, respectively) are lower than those produced from direct precipitation. Without further research on, and optimization of, red cake precipitation, or further upgrading of the red cake produced, it would be unlikely that these low grade precipitates would be saleable.

After adjusting the pH of the oxidized molybdenum removal solution for Test 3, a bright orange solid began to precipitate from solution. After 1 h at either pH 1.5 or pH 2, almost 99% of the vanadium in the solution had been precipitated, with the final precipitates grading 73.0% V_2O_5 for pH 1.5 and 76.5% V_2O_5 for pH 2.0. The precipitate was essentially free of all impurities analyzed, with only small amounts of K and Mo being the only elements detected. It is possible that this precipitate is "orange cake", a sodium ammonium vanadate compound analyzing, approximately, $(NH_4)_4Na_2V_{10}O_{28}\cdot 15\,H_2O$, which usually has a grade of 68 to 75% V_2O_5 and is sold commercially as a vanadium byproduct by some vanadium producers (246). It is likely that residual ammonium ions from the molybdenum precipitation, combined with the high $NaClO_3$ addition during oxidation, led to the formation of this alternate vanadium product. After calcining this precipitate at 500°C, the vanadium grade of the precipitate was increased to between 83 and 86% V_2O_5.

9.2.2.1 Detailed Analyses of Solids and Solutions

Detailed solid and solution analyses from Test 2 are shown in Table 9.8.

Table 9.8 Detailed Analyses from Molybdenum Removal Test 2

	Solution Analysis, mg/L						Solids Analysis, %
	Leach		Mo Removal		Precipitation		
	Filtrate	Wash	Filtrate	Filtrate*	Filtrate	Filtrate*	V Precipitate
Analysis							
Al	9.3	1.2	5.7	10.6	2.4	7.7	<0.01
Cd	9.4	0.5	0.2	0.3	0.1	0.3	<0.01
Ca	662	394	296	549	183	578	0.16
Cr	0.9	0.8	1.2	2.3	0.6	1.9	0.02
Co	8.1	1.6	1.2	2.1	0.8	2.4	<0.01
Cu	0.9	0.1	0.1	0.3	0.2	0.6	<0.01
Fe	4.2	<0.1	3.5	6.4	2.4	7.7	0.37
Pb	<0.1	<0.1	1.1	2.0	0.6	2.0	<0.01
Mg	73.1	24.2	100	186	69.6	220	1.03
Mn	248	21.9	163	302	85.3	270	0.07
Mo	458	34.2	1.70	3.2	<0.1	<0.1	0.05
Ni	42.9	5.7	7.0	12.9	4.6	14.5	0.04
Si	86.9	9.7	37.7	70.0	22.6	71.6	<0.01
Ag	31.0	0.7	0.4	0.8	1.0	3.1	0.01
Ti	8.1	13.0	5.0	9.3	0.0	0.0	<0.01
V	14400	1410	6790	12600	137	432	37.6
V_2O_5	25600	2510	12100	22400	243	769	66.9
Zn	16.2	1.2	4.1	7.5	3.0	9.4	0.02

* Corrected for evaporation/dilution

The major impurities in the red cake, as in the red cake from direct precipitation, are Ca, Fe, Mg and, likely, Na, with concentrations ranging from 0.2 to 1.0%. (There are higher concentrations of Mg and lower concentrations of Ca in the molybdenum-free precipitate than in the direct precipitate.) Precipitation of most other impurities is low or negligible, even for elements like Mn or Si, that are in relatively high concentrations in the molybdenum removal solution. The high concentrations of impurities, such as Ca and Mg, in the red cake, despite relatively low concentrations in the solution is troublesome, as both of these elements, as well as sodium, would be very difficult to remove from solution without the use of solvent extraction or ion exchange.

Elements that readily form sulphides, such as Ag, Co, Ni and Zn, were precipitated to varying degrees along with molybdenum during sulphidation.

9.3 Ammonium Metavanadate Precipitation

Ammonium metavanadate precipitation is the main process used by primary vanadium producers for the recovery of vanadium from salt roast leach solutions. The high purity of this product allows it to be used directly as a catalyst or in ferrovanadium or nonferrous vanadium alloy production. High purity vanadium pentoxide derived from ammonium metavanadate is also the proposed source of vanadium for producing vanadium electrolyte for the vanadium redox battery (VRB). Silicon is the only detrimental impurity noted by researchers of the VRB, with difficulties arising when V_2O_5 contains more than 0.1% Si.

Though silicon concentrations in leach solutions from salt roasting titanomagnetite ores are not well documented in the literature, virtually all of the vanadium producers in South Africa and Australia use a desilication step to lower the silicon levels in solution before precipitating ammonium metavanadate. Generally, aluminum sulphate is added to the leach solution, which is then heated to precipitate a filterable natroaluminosilicate sludge, which results in the loss of the some of the vanadium values in the leach solution.

9.3.1 Desilication

The solution from salt roasting of oil sands fly ash already contains low levels of silicon (V:Si commonly of 100 to 140), but desilication was included before ammonium metavanadate precipitation to try to produce a very low silicon vanadium pentoxide precipitate.

Scoping tests were initially performed to identify pH conditions and alum additions for larger scale desilication tests. Alum addition to solutions of pH 3, 5 and 7 did not form any sort of precipitate, but silicon was precipitated from solutions at pH 9 or 11 when alum was added. (The pH of most water leach solutions from this testwork varied

between 6.2 and 6.8.) Higher alum additions were required at pH 9 to produce a silicon-containing precipitate than at pH 11 (2:1 and 1:1 Al:Si mole ratio, respectively). Desilication increased the V:Si weight ratio from 105:1 in the leach solution to 265:1 (pH 9) and 500:1 (pH 11). Vanadium losses were estimated to be 4 and 6% at pH 9 and pH 11, respectively.

The table below summarizes the results from the larger scale desilication tests. Slightly higher alum additions were used in these tests to try to further increase the V:Si weight ratio in the desilication solutions.

Table 9.9 Summary of the Results of Desilication Tests

Precipitation pH	pH 9	pH 11	pH 10
$Al_2(SO_4)_3 \cdot 18\ H_2O$ Addition, g	0.75	0.5	1.05
Al:Si Mole Ratio	3.1	1.8	5.3
V:Si Weight Ratio			
Leach Solution	122:1	106:1	151:1
Solution after Desilication	234:1	1150:1	1310:1
Precipitation, %			
V	3.2	4.3	7.3
Fe	50.5	78.2	82.6
Mo	0.5	0.0	0.0
Ni	82.5	98.2	97.1
Si	55.3	92.5	91.3
Ti	42.3	72.4	94.3

The efficiency of desilication increases significantly with increased pH and, less notably, with increased alum addition. However, both increasing pH and increasing alum addition also appear to increase vanadium losses, with high alum additions having the greater effect on vanadium losses. Higher V:Si ratios were possible at the higher pH at lower alum additions, while also removing more Fe, Ni and Ti from solution. At present, desilication at pH 10 or 11 with low alum additions would appear to the most attractive option for producing a high purity vanadium product.

Based on the low silicon contents of the V_2O_5 precipitates produced in this testwork, it is expected that a V:Si ratio in the desilication of 500:1 to 1000:1 would be acceptable to

produce a vanadium product containing less than 0.1% Si. Thus, it is likely that, with optimization of precipitation pH and alum addition, the vanadium losses in the desilication residues can be lowered to around 1 to 2% of the soluble vanadium while still lowering silicon to acceptable levels. Optimization to lower alum additions could also be necessary as excess aluminum in the desilication solutions at higher pH caused contamination of the vanadium precipitate.

Recycling of the desilication residue to salt roasting may also be a possibility, as the aluminosilicate residue formed may respond similarly to the aluminosilicates in the fly ash to salt roasting at the low roasting temperatures used. Further research would be required to determine the roasting response of, and possibility of vanadium recovery from, the desilication residues.

9.3.2 Vanadium Precipitation

The results from the three ammonium metavanadate precipitation tests performed are given in Figures 9.10 and 9.11. Analyses of the solids produced in these tests are shown in Figure 9.12. The precipitation of V, Mo and Ni in desilication and precipitation are reported as percentages of these elements in the feed solutions to those unit operations (the leach and desilication solutions, respectively), and also as their overall precipitation (distribution), relative to their initial concentrations of these elements in the leach solutions.

The first two tests used two stages of NH_4Cl addition, with an excess of 3.5 and 1.2 times stoichiometric added in Stages 1 and 2, respectively, with more ammonium metavanadate being precipitated with higher additions. Based on the results of Test 3, where a higher first stage NH_4Cl addition was used (excess of 3.9 times), it expected that higher NH_4Cl additions will generally result in higher vanadium precipitation efficiencies.

The low vanadium concentration in the leach and desilication solutions (22.5 to 23.6 g/L V_2O_5) greatly increases the amount of NH_4Cl required to achieve high precipitation

Table 9.10 Results of Ammonium Metavanadate Precipitation at pH 9 and pH 11 (Tests 1 and 2)

Precip. pH	pH 9				pH 11			
Solution Sample	Leach	Desili-cation	Precipitation Stage 1	Precipitation Stage 2	Leach	Desili-cation	Precipitation Stage 1	Precipitation Stage 2
Analysis								
Al, mg/L	0.8	2.5	<0.1	<0.1	4.9	33.0	7.0	3.2
Fe	2.4	1.3	0.5	0.5	4.8	1.2	0.7	0.5
Mo	252	204	162	102	410	336	238	98.0
Ni	4.7	0.9	0.2	0.1	52.0	1.1	<0.1	0.5
Si	116	56.8	16.2	16.5	135	11.6	2.4	3.6
Ti	1.9	1.2	<0.1	<0.1	6.0	1.9	<0.1	<0.1
V	14100	13300	2960	610	14300	13300	4080	1110
V_2O_5	25100	23600	5300	1090	25400	23600	7260	1970
Extraction, %	77.0				78.1			
Precipitation, %								
Mo		0.5	19.0	46.4		0.0	31.0	70.0
Ni		96.9	78.0	88.3		71.1	>99.9	n.a.
V		3.2	77.8	95.1		4.3	70.3	89.5
Distribution, %								
Mo		0.5	18.9	27.3		0.0	31.0	39.0
Ni		96.9	2.5	0.3		71.1	28.9	0.0
V		3.2	75.2	16.8		4.3	67.3	18.4

Table 9.11 Results of Ammonium Metavanadate Precipitation at pH 10 (Test 3)

	Leach Solution	Desilication Filtrate	Precipitation Filtrate	
			Stage 1	Mo Removal
Solution Analysis				
Al, mg/L	6.1	32.2	13.8	8.6
Fe	3.9	0.8	<0.1	<0.1
Mo	287	286	170	0.3
Ni	26.4	0.9	<0.1	0.9
Si	94.0	9.7	2.4	4.0
Ti	4.4	0.3	<0.1	<0.1
V	14200	12700	384	364
V_2O_5	25200	22500	684	648
Extraction, %	77.4			
Precipitation, %				
Mo		0.0	38.4	99.9
Ni		>99.9	n.a.	n.a.
V		7.3	96.9	97.6
Distribution, %				
Mo,%		0.0	38.4	61.5
Ni		>99.9	n.a.	n.a.
V		7.3	89.8	0.7

Table 9.12 Solids Analyses for Ammonium Metavanadate Precipitation Tests

Precip. pH	pH 9				pH 11				pH 10		
	Desilic. Residue	Vanadium Precipitate			Desilic. Residue	Vanadium Precipitate			Desilic. Residue	V Precipitate	
		Stage 1	Stage 1*	Stage 2		Stage 1	Stage 1*	Stage 2[1]		Stage 1	Stage 1*
Analysis, %											
Al	9.83	0.06	<0.01	0.04	2.65	0.12	0.14	0.55	5.55	0.26	0.21
Fe	0.14	0.04	<0.01	0.04	0.08	<0.01	<0.01	<0.01	0.08	0.04	<0.01
Mo	0.04	0.08	0.06	0.08	0.00	<0.01	0.02	0.18	<0.01	<0.01	0.02
Ni	0.15	<0.01	<0.01	<0.01	0.55	<0.01	<0.01	0.05	0.40	<0.01	<0.01
Si	2.04	0.30	0.13	0.26	1.76	0.21	0.08	0.23	1.44	0.19	0.06
Na	n.a.	<0.01	0.16	<0.01	n.a.	<0.01	0.15	<0.01	n.a.	<0.01	0.33
Ti	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	<0.01	<0.01
V	15.1	43.4	54.4	43.6	9.11	44.0	54.0	36.2	18.4	41.2	47.2
V_2O_5	26.9	77.3	96.8	77.6	16.2	78.3	96.1	64.4	32.8	73.3	84.0
Wt. Loss, %		75.5	n.a.	72.7		75.7				74.2	

* Calcined precipitate

[1] Orange precipitate produced (likely sodium ammonium vanadate)

efficiencies (19,39). In commercial practice, several techniques are used to concentrate vanadium to around 55 to 70 g/L V_2O_5 in the solution prior to precipitation to lower the plant size and required additions of ammonium salts (19). These techniques include maintaining high pulp densities in leaching, often by leaching directly in a SAG type mill, quenching of hot calcine in recirculated leach liquor to evaporate water, and using evaporators to concentrate the final liquor. It is conceivable that similar techniques could be used in a plant producing vanadium from oil sands fly ash. Thus, further precipitation testwork to optimize the precipitation conditions and NH_4Cl additions would be best done on more concentrated vanadium solutions.

High grade ammonium metavanadate precipitates were achieved at pH 9 and pH 11, with 77.3 and 78.3% V_2O_5 analyzed. From stoichiometry, pure ammonium metavanadate should contain 77.4% V_2O_5, but a sample of reagent grade ammonium metavanadate of analyzed 79.5% V_2O_5, indicating that high purity ammonium metavanadate normally has a higher than stoichiometric vanadium content. After calcining these precipitates to drive off ammonia, the final V_2O_5 grade of the precipitates was 96.8 and 96.1%, with the major impurities, of those analyzed, being Si (0.08 to 0.13%), Na (0.15 to 0.16%), Mo (0.02 to 0.06%), and, at pH 11, Al (0.14%). These V_2O_5 grades are lower than the minimum grade for V_2O_5 (98.5%), but the very low sodium and silicon content of the V_2O_5 from these solutions may still make these precipitates attractive for ferrovanadium or vanadium metal production.

Lower grade precipitates were also produced in some of these tests. In Test 3, a lower grade ammonium metavanadate precipitate was formed (73.3% V_2O_5). This is believed to be a result of contamination of the precipitate with NH_4Cl, due to the very high single stage NH_4Cl addition used in that test. As well, adjustment of the pH to pH 11 in the second stage of Test 2 before adding additional NH_4Cl resulted in the formation of a lower grade orange precipitate (presumably, orange cake ($(NH_4)_4Na_2V_{10}O_{28}\cdot 15\ H_2O$). Without this pH adjustment, it is expected that more ammonium metavanadate would have been precipitated to give similar levels of vanadium precipitation as at pH 9. With

proper control and optimization of precipitation, it is expected that the formation of these low grade precipitates can be eliminated.

Overall, relatively high grade ammonium metavanadate was produced without significant optimization of the desilication or precipitation steps. With further research and optimization, it is expected that further improvements in the precipitation efficiencies and product grade could be made to produce V_2O_5 containing greater than 98.5% V_2O_5. (Solvent extraction would likely still be required to produce high purity reagent grade V_2O_5 (>99.5%) from these leach liquors.) Due to current trends towards marketing of extremely high grade vanadium products, and the improved precipitation efficiencies and product purities for ammonium metavanadate precipitation, compared with red cake precipitation, achieved in this testwork, AMV production would be preferred over red cake precipitation for recovering vanadium from oil sands fly ash solutions.

Molybdenum removal from the barren liquor from ammonium metavanadate precipitation was also performed in Test 3. Near quantitative precipitation of molybdenum was possible at much lower $(NH_4)_2S$ additions than required in acidic solution. (Sulphide ions are stable at high pH, thus limiting the formation of S° or polysulphides, and reducing the amount of excess reagent required.) However, as is common in sulphide precipitation at high pH, the molybdenum precipitate produced was extremely fine and, therefore, difficult to recover by direct filtration of the solution. Several options could be tested to improve the filtration properties of the molybdenum precipitate, including using flocculants to agglomerate the precipitate and improve filtration, recycling of the precipitate or increasing solution temperature to encourage particle growth and increasing particle size through more controlled precipitation using H_2S and a solids recycle. Thus, it may be possible to produce a saleable molybdenum byproduct while removing it as an impurity from the precipitation solutions.

9.4 Conclusions

Vanadium can be recovered from leach solutions, either as red cake or as ammonium metavanadate. Both types of precipitation were tested for the leach solutions from salt roasting of oil sands fly ash.

Direct precipitation of red cake from the leach liquors produced red cake generally grading between 76 and 82% V_2O_5 with precipitation efficiencies ranging from 92 to 98%. (For more concentrated solutions, longer precipitation times were required to achieve high precipitation efficiencies.) The red cake from these tests also contained 1 to 2% Mo, which could reduce the marketability of this as a vanadium product.

Up to 99% of the molybdenum could be removed from the leach liquor by acidification and sulphidation to precipitate an impure molybdenum sulphide. Vanadium losses in molybdenum removal varied from 0.2 to 11.5%, but could likely be minimized with further optimization. Oxidation of the molybdenum removal solution, at times, proved difficult and, in several cases, caused difficulties in subsequent precipitation of vanadium. Generally, though, 90 to 97% of the vanadium in the molybdenum free solution could be precipitated to produce red cake grading between 69 and 79% V_2O_5. However, the low grades of the red cake produced, and the variability in those grades from test to test, would likely make recovery of vanadium as red cake unattractive economically.

Ammonium metavanadate precipitation was also tested. Desilication of the leach liquor, by raising the pH and adding alum, was shown to be most effective at higher pH (pH 10 to 11) with low alum additions. Relatively pure ammonium metavanadate precipitates, containing 77.3 to 78.3% V_2O_5, were produced during precipitation, which correspond to calcined V_2O_5 grades of 96.1 to 96.8% V_2O_5. Additions of NH_4Cl well in excess of stoichiometric requirements were necessary to achieve high precipitation efficiencies, but it is expected that concentration of the leach liquor, using evaporation, could significantly lower the required additions of NH_4Cl.

Further optimization of ammonium metavanadate precipitation would be required to improve the grades of the precipitates produced and to optimize desilication conditions and NH_4Cl additions, but the high grade of the precipitates produced in this testwork would make precipitation of ammonium metavanadate a much more attractive option for recovering vanadium from oil sands fly ash than precipitation of red cake.

10.0 Process Flowsheet Development and Future Work

The development of an integrated process flowsheet for vanadium recovery from oil sands fly ash is critical to be able to identify areas for further research and, move towards commercial production of vanadium from these materials closer to reality. Based on the research in this study, a conceptual process flowsheet has been proposed and is discussed in Section 10.1. Future work to determine the feasibility of this flowsheet, and to answer other questions raised by this research, is proposed in Section 10.2.

10.1 Process Flowsheet

A conceptual process flowsheet for recovering vanadium from Suncor fly ash is shown in Figure 10.1. (A rough mass balance for this flowsheet is provided in the appendix.) For the most part, this process resembles that of a typical vanadium recovery plant, such as those operating in South Africa or Australia. However, there are several distinct differences in the process flowsheet proposed for treating oil sands fly ash.

The first major difference is in the roasting conditions proposed. Roasting with NaCl is shown to be the best overall reagent for recovering vanadium from Suncor fly ash. As well, roasting with NaCl, instead of Na_2SO_4, has several advantages as it eliminates the formation of SO_2 during roasting and lowers the roasting temperatures required for high recoveries. The lower temperatures will significantly lower energy costs in roasting, relative to the costs of roasting vanadiferous magnetite ores. The lower roasting temperature will also reduce the available waste heat when the calcine is cooled, but some of this waste heat could likely be made up from cooling the off gases from decarbonization.

The second major difference is the proposed production of NH_4Cl from roaster off gases. Based on previous, and current, observations made during salt roasting of oil sands fly ash, it is believed that HCl is produced during roasting from NaCl, not Cl_2. This gas

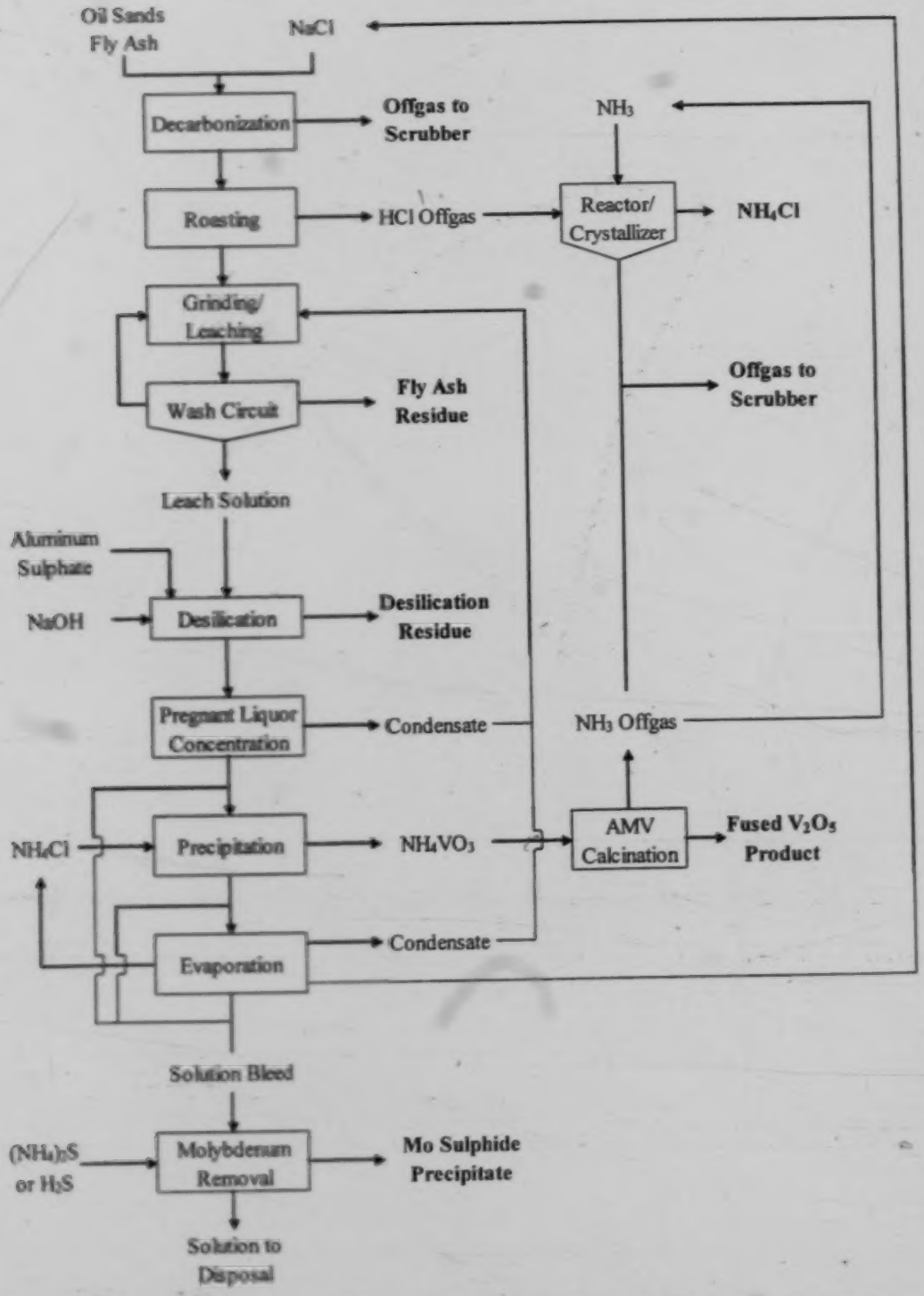


Figure 10.1 Proposed Process Flowsheet for Vanadium Production from Suncor Fly Ash

would have to be scrubbed from the roaster gas and, based on the amount of sodium in the leach solutions, this would require scrubbing of over 150 kg of HCl for every tonne of decarbonized fly ash being treated by salt roasting. If not utilized, this would represent a significant volume of acidic effluent, which would have to be neutralized prior to disposal.

Ammonium chloride has been successfully produced by contacting a diluted HCl gas stream with ammonia in Brazil in the early 1970's (247). It is expected that a similar flowsheet could be used directly on the salt roasting off gas to eliminate scrubbed HCl as an effluent stream and produce NH_4Cl. Some of this NH_4Cl could be used in ammonium metavanadate precipitation, while the rest could be sold, depending on the market for ammonium chloride as a chemical reagent or fertilizer. Based on a preliminary mass balance, roughly 200 kg of surplus NH_4Cl per tonne of decarbonized ash could be produced as a saleable byproduct of vanadium production. At current vanadium prices ($2.64 to $2.95 per kilogram), the value of the NH_4Cl produced could actually exceed the value of vanadium produced from the fly ash (248). At higher vanadium prices, the relative contribution of ammonium chloride to total revenue would decrease, but it would still represent a significant source of revenue for a proposed vanadium plant. Production of ammonium chloride also represents a major chloride bleed, thus, minimizing the need to treat other process solutions to remove chloride from the system.

Third, the high pH (pH 9 to 11) required for desilication of and AMV precipitation from the oil sands fly ash leach liquor could be used to provide an additional benefit to the vanadium recovery process, by providing a bleed for numerous elements, such as Fe, Mn, Ni, Ti and Si, which could otherwise build up as plant solutions are recycled. These elements could then be bled and disposed of along with the desilication residue.

Fourth, evaporation of the barren liquor from precipitation to recover both NaCl and NH_4Cl from solution is another departure from standard vanadium plant practice, which instead usually employs the crystallization of sulphate salts. Based on the available literature (249) and the $NaCl:NH_4Cl$ ratio expected in the barren liquor, good control of

the evaporation of the barren liquor would allow for the crystallization of NaCl from solution at the evaporation temperature (100°C) and secondary crystallization of NH_4Cl from the solution on cooling to room temperature. The evaporation and cooling path proposed for the precipitation solution for this process is shown on Figure 9.5. (Cooling of the evaporated solution would likely result in partial precipitation of NH_4VO_3 from solution, which would contaminate the NH_4Cl produced in this step.) However, the recycle of NH_4Cl, and any precipitated ammonium metavanadate, to precipitation would, not only, make more efficient use of the NH_4Cl added initially in precipitation, but would also allow recovery of any NH_3VO_3 precipitated during NH_4Cl crystallization as well as residual vanadium that was not recovered in the first pass through precipitation.

The NaCl:NH_4Cl ratio in the solution after one pass through evaporation indicates that this solution could be further evaporated to precipitate additional NaCl and NH_4Cl. Hence, the solution leaving the evaporation circuit could be recycled and further evaporated to achieve high overall recoveries of NH_4Cl and NaCl from solution. Thus, not only high recoveries of NH_4Cl and vanadium could be achieved, but NaCl recovery could reduce the requirement for fresh NaCl to salt roasting by about 10%, as well as providing a major bleed for sodium from the process solutions.

Finally, a bleed from evaporation would also be necessary to control the buildup of molybdenum and other elements in the evaporation solution. This should improve the economics of molybdenum precipitation as it would allow precipitation from a small volume of high grade molybdenum solution, rather than a large volume of dilute solution, as previously proposed and tested. Though the volume of molybdenum sulphide produced would be low, it may be possible to market this product, or another byproduct, such as MoO_3, as an additional source of revenue to a proposed vanadium plant. The solution after molybdenum removal could then be neutralized with lime to precipitate any remaining metals before disposal.

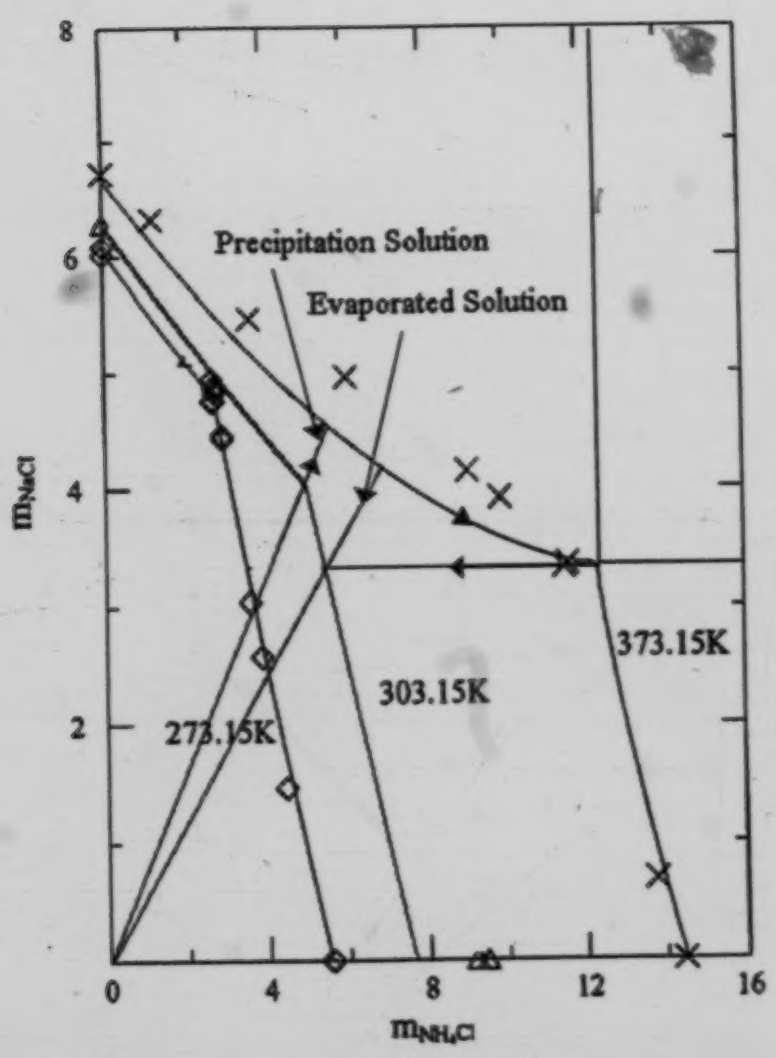


Figure 10.2 Solubilities in the Ternary $NaCl$-NH_4Cl-H_2O System (249)

The feasibility of evaporation circuit in this flowsheet would be dependent on capital and operating costs and other economic considerations. However, the recycle of water as a relatively pure condensate to leaching would minimize the requirements for fresh process water, and would also significantly reduce the amount of liquid effluent produced by the proposed plant. Based on this flowsheet, the major waste products from this plant would be the off gases from decarbonization (i.e., CO_2 and minor amounts of SO_2) and the well-washed solid residues, such as the roast/leach residue and desilication residue. Eventually, the roast/leach residues would be expected to weather to produce clays and

the low concentrations, and solubilities, of most deleterious elements would make leaching of harmful elements from this residue unlikely. Alternatively, the roast/leach residues may be marketable as a low cost additive in concrete or for road construction. Further research into the use of the residue in these applications would be required.

Production of high purity, reagent grade vanadium pentoxide may still require the integration of a solvent extraction circuit into the proposed flowsheet. This would require rerouting of several of the solution streams through the precipitation, evaporation and solution bleed circuits to maintain high recoveries of V, NaCl, NH_4Cl and Mo in the overall flowsheet.

10.2 Future Work

Additional testwork will be required before a vanadium plant in Fort McMurray could be constructed. However, this testwork is beyond the scope of this project and would likely require miniplant testing of the roasting and leaching flowsheet, to generate large volumes of solutions and solids for further testing.

Several areas would require further study to determine their effect on overall vanadium recovery and to be able to make decisions on the details of a final vanadium recovery flowsheet. These areas include:

- integration of the treatment of Syncrude ash with vanadium production from Suncor ash,
- optimization of the desilication process to minimize vanadium losses and maximize the precipitation of silicon and other significant impurities,
- optimization of ammonium metavanadate precipitation to produce a higher grade vanadium precipitate,
- minor element deportment, especially through desilication, precipitation, and evaporation/crystallization, with special attention paid to the extensive recycling of solutions in this flowsheet,
- testing of the evaporation/crystallization flowsheet, with special attention to the effects and deportment of elements, such as Ca, Mg, K, on NaCl and NH_4Cl crystallization,
- optimization of molybdenum removal from the higher concentration evaporation bleed solution,
- testing to confirm the feasibility of NH_4Cl production from the off gas from salt roasting,
- investigation into the feasibility of externally firing the kilns for salt roasting (i.e., to minimize the amount of water vapor in the roaster gases), and
- investigation into the possibility of recovering vanadium from desilication sludge with salt roasting to reduce vanadium losses in the proposed flowsheet
- investigation into the feasibility of using roast/leach residue as an additive in concrete or for road construction

Second, additional research could also be conducted in several other areas to investigate alternatives to the proposed process flowsheet. These areas include:

- optimization of grinding and magnetic separation to determine the feasibility of recovering an Fe-Ti-Ni concentrate from the roast/leach residue,
- further roasting tests on the effect of CaO as a roasting additive to investigate CaO roasting as an alternative to salt roasting,
- further roasting tests to determine the effectiveness of potassium salts as alternative roasting reagents to NaCl, and
- testing to determine the effects of Na_2CO_3 leaching on ammonium metavanadate precipitation and on the proposed evaporation/crystallization flowsheet

Finally, completion of feasibility and engineering studies would be required to determine the economic feasibility of the various unit operations that have been proposed, and of a commercial plant for production of vanadium from oil sands fly ash.

11.0 Conclusions

Oil sands fly ash represents a significant potential resource for vanadium production in northern Alberta. Significant inroads were made in this research towards the development of a process flowsheet for commercial production of vanadium from these waste materials.

First, the variability in the Suncor ash feedstock with time was studied, and roasting and leaching conditions were optimized to produce maximum vanadium extractions from all the ash samples tested. Alternative roasting reagents were screened, to try to improve vanadium extractions, and some possible alternatives to NaCl were identified. Alternative lixiviants were also tested, with some reagents showing good selectivity towards vanadium and higher vanadium extractions than possible with water leaching. High grade vanadium precipitates were produced at high precipitation efficiencies from the salt roast leach liquors. Finally a conceptual process flowsheet was developed which should allow for high recoveries of V, NaCl, NH_4Cl and Mo for a proposed vanadium production plant.

Second, the response of Syncrude fly ash to salt roasting and leaching was also documented and modifications to the conditions proposed for treatment of the Suncor ash were made to maintain high vanadium recoveries from these materials. The Syncrude ash was shown to be much more variable than the Suncor ash, making it a less attractive potential feed for vanadium production.

Finally, characterization tests, including x-ray diffraction, scanning electron microscopy, and diagnostic leaching tests, were also performed on the roasted and unroasted oil sands ash samples. For the first time, a good understanding of the mechanism behind the salt roasting of the oil sands fly ash, especially for the Suncor ash was attained. The extent of vanadium extraction was found to be closely related to the type of aluminosilicate minerals formed during roasting. Thus, this improved understanding of the reaction mechanisms involved in vanadium recovery could lead to future improvements and optimization of vanadium extraction from these materials.

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APPENDIX

Assumptions for Mass Balance

Parameters	Value	Units
V in decarbonized fly ash	3.25	wt%
Mo in decarbonized fly ash	0.15	wt%
Vanadium Extraction	80	%
Molybdenum Extraction	30	%
Salt Addition	25	%
Weight gain during roasting	2	%
NaCl Reporting to Solution	10	% of total
NaCl Molar Mass	58.44	g/mol
NH_4Cl Molar Mass	53.5	g/mol
V Loss in Desilication	2	% of V in leach solution
V in Desilication Residue	10	wt% V
V Concentration in Pregnant Liquor	60	g/L
Precipitation Efficiency (V)	95	%
Ammonium Metavanadate Purity	98.5	%
V in Pure Ammonium Metavanadate	78.5	%
Excess NH_4Cl to Precipitation	100	%
NH_4Cl Recycle	50	% of NH_4Cl to circuit
Mo Bleed	15	% of evaporation solution
Mo Precipitation	99	%
Mo Precipitate Grade	60	% Mo
Basis for Mass Balance	1	tonne of decarbonized ash

Assume that: 1) Evaporation during leaching is equivalent to the water added to wash the leach residue
2) NaCl and NH4Cl follow the solubility curve given by Ji, et al. (249)

Mass Balance of Proposed Flowsheet for Vanadium Recovery from Oil Sands Fly Ash

	Mass	Volume	Mass, kg				Concentration			
	kg	L	V	NaCl	Mo	NH_4Cl	V	NaCl	Mo	NH_4Cl
Feeds										
Decarbonized Fly Ash	1000		32.5		1.5		3.25		0.15	
Salt	250			250				100		
Roasting/Leaching										
Leach Solution		1000	26.0	25.0	0.45		26.0		0.45	
Leach Residue	1020		6.5		1.05		0.64		0.01	
Desilication										
Desilication Solution		1000	25.5	25.0	0.45		25.5		0.45	
Desilication Residue	5.2		0.5				10.0			
NH_4Cl from HCl offgas						207				99.5
Precipitation										
Pregnant Liquor		424.7	25.5	25.0	0.45		60	58.9	1.06	
Fresh NH_4Cl Addition	26.8					26.8				
NH_4Cl Recycle	26.8		1.27			26.8				
Barren Liquor		424.7	1.27	25.0	0.45	26.8	3.00	58.9	1.06	63.0
Ammonium Metavanadate	58.7		25.5				43.4			

Mass Balance of Proposed Flowsheet for Vanadium Recovery from Oil Sands Fly Ash (Cont'd)

	Mass	Volume	Mass, kg				Concentration			
	kg	L	V	NaCl	Mo	NH_4Cl	V	NaCl	Mo	NH_4Cl
Evaporation										
Evaporation Feed		493.9	1.34	38.5	3.03	45.5	2.7	78.0	6.13	92.2
Evaporation		149.6	1.34	38.5	3.03	45.5	9.0	257.6	20.2	304.2
NaCl Crystallization Sol'n		69.2	1.34	13.5	3.03	45.5	19.4	195.8	43.8	658.1
NaCl	25.0			25.0						
NH_4Cl Crystallization Sol'n		69.2	0.07	13.5	3.03	18.8	1.0	195.8	43.8	271.2
$NH_4Cl + (NH_4VO_3)$	28.0		1.27			26.8				
Mo Bleed										
Bleed Solution		10.4	0.01	2.03	0.45	2.81	0.97	195.8	43.8	271.2
Mo Precipitate	0.7				0.45					
Mo Free Solution		10.4	0.01	2.03	0.00	2.81	0.97	195.8	0.44	271.2

Reagent Costs for Proposed Vanadium Recovery Plant

Additives	kg	$/tonne	Cost ($US)
NaCl	225.0	65	$14.63
Ammonia	65.6	295	$19.35
NaOH	0.013	600	$0.01
Aluminum Sulphate	4.7	206	$0.98
Total (1 tonne Basis)			$34.96
Total (Daily Production)			$5,910

Sources of Revenue for Proposed Vanadium Recovery Plant

Assumption: Current vanadium price ($1.20/lb)

Products	kg	$/kg	Price ($US)
V_2O_5	44.9	2.64	$118.5
NH_4Cl	180.3	0.80	$144.2
Total (1 tonne Basis)			$262.7
Total (Daily Production)			$44,400

Assumption: Vanadium price ($2.40 lb)

Products	kg	$/kg	Price ($US)
V_2O_5	44.9	5.28	$237.1
NH_4Cl	180.3	0.80	$144.2
Total (1 tonne Basis)			$381.3
Total (Daily Production)			$64,400

* Reagent and NH_4Cl prices from Camford Chemical Report/Chemical Prices (248)